The Crystal Structure of Some Disaccharides.

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SUMMARY

The crystal structures of α,α-trehalose dihydrate and 4,6;4',6'-di-O-ethylidene-α,α-trehalose monohydrate have been determined by X-ray diffraction techniques. In both cases three-dimensional X-ray intensity data were collected using an equi-inclination Weissenberg camera with Cu K_α radiation. The intensity measurements were made visually.

α,α-trehalose dihydrate was found to be orthorhombic, space group $P2_12_12_1$, with a = 12.233 Å, b = 17.889 Å, c = 7.596 Å and Z = 4. The observed and calculated densities were 1.512 and 1.511 $g.cm^{-3}$ respectively. The structure was solved by direct methods using the tangent formula. The atomic parameters were refined by the method of least squares to a final residual, R = 5.5%.

It was found that the molecules are held together by van der Waal's forces and by a complex network of twelve hydrogen bonds. One water molecule is trigonally and one tetrahedrally co-ordinate. The acetal oxygen atom in one residue only acts as an acceptor in a hydrogen bond, which is rather long at 2.88 Å. The molecule is in the expected conformation with the two glucopyranose rings in the "chair" form. The bond angle at the glucosidic linkage is 115.7°. The two crystallographically unrelated but chemically identical glucose residues are closely similar. The main effect of the different crystal packing of the two rings is to cause slight distortions of the atoms O(3) and O(4).

4,6;4',6'-di-O-ethylidene-α,α-trehalose monohydrate was found to be monoclinic, space group $P2_1$, with a = 11.276 Å, b = 8.435 Å, c = 10.004 Å,

$\beta = 97.58^{\circ}$ and $Z = 2$. The observed and calculated densities were 1.452 and 1.445 $g.cm^{-3}$ respectively. The structure was solved by direct methods using the Σ_2 relationship. The atomic parameters were refined by the method of least squares to a final residual, R = 12.2%.

It was found that the molecules are held together by a network of six hydrogen bonds and by van der Waal's forces which were particularly strong between the methyl groups. The water molecule is trigonally co-ordinate. Two ethereal oxygen atoms act as acceptors in hydrogen bonds, which are both rather long at 2.83 and 2.88 Å. The six-membered rings closed by the ethylidene group are parallel to the glucopyranoid rings and in the chair form. The methyl groups are in the equatorial position. The bond angle at the glucosidic linkage is 115.0°. The stereochemistry of this linkage is very similar to that in the α,α-trehalose molecule.

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INTRODUCTION

(a) Carbohydrates and Crystallography.

The carbohydrates constitute one of the most important classes of organic compounds both in theory and in practice. Their part in the chemical processes which take place in living organisms is of the utmost importance. In this respect, only the proteins may be said to surpass them. In consequence of the importance and diversity of the carbohydrates, a great volume of chemical information about them has been collected since the classical work of Fischer, Purdie, Haworth and Irvine first established this field of chemistry. On the other hand, at the time when the studies described in this thesis were commenced, few determinations of the crystal structures of carbohydrates had been reported in the literature. In recent years much more attention has been paid to stereochemistry and structure in organic chemistry, especially in the field of natural products. There has , therefore, been an increasing number of crystallographic carbohydrate structure determinations.

In contrast to the proteins, which are often obtained in the form of good single crystals, the carbohydrates are generally only partially ordered, and are often completely amorphous. This is because the function of a protein may be quite precise, requiring each molecule to have exactly the same stereochemistry. Polysaccharides, however, have less demanding functions, e.g. as the material of cell walls, so that molecular uniformity is not required. At the best, then, a polysaccharide may exist in the form of fibres, in which many identical helical strands are bundled together in a disordered fashion. X-ray diffraction photographs of the

fibres may lead to the establishment of the approximate geometry of the helical repeat unit, but in order to achieve this it is necessary to have accurate knowledge of the structures of the sugar units of which the polymer is constituted, since model-building is an essential part of such studies.

In order to describe completely the structure of any polysaccharide, the following features must be specified:

(i) the sequence of the sugar units;

(ii) the ring size in the sugar units;

(iii) the conformation of the sugar units;

(iv) the positions of the bonding between adjacent units;

(v) the size of the bond angle at the linkage between units;

(vi) the torsion angles about both of the two bonds involving the oxygen atom in the linkage.

The first four of these are within the scope of the physical and biochemical methods of the sugar chemist, although it should be mentioned that the ways of determining conformations have been proven by X-ray diffraction studies. The stereochemistry of the sugar linkage is, however, a much more difficult problem.

The bond angle at a glycosidic oxygen atom has been evaluated in several studies of disaccharides, and for one trisaccharide, raffinose (H. M. Berman, 1970). The values obtained range from about 111° to 122°, in the melibiose and sucrose portions of raffinose. The average value for the bond angle at a glycosidic oxygen atom is about 117°.

The conformation about the C(1) - O(1) bond is often dominated by the exo-anomeric effect (A. J. de Hoog, H. R. Buys, C. Altona and E. Havinga, 1969). In any moiety C - X - C - Y there are interactions favouring a gauche conformation, but these interactions are very weak, of the order of 1 or 2 kcal $mole^{-1}$. These authors concluded that more experimental evidence was needed so that better empirical rules could be formulated.

In a disaccharide molecule it is often possible for an internal hydrogen bond to exist between one of the hydroxyl groups in one sugar unit and the ring oxygen atom in the other. In crystal structures, however, such a bond is not found. When a ring oxygen atom does participate in a hydrogen bond, it is either to a water molecule, as in raffinose, or to a hydroxyl group in a different molecule. Since naturally occurring sugars are found in aqueous media, it may be speculated that this hydrogen bonding will be to water molecules rather than internally. The internal bond imposes a constraint on the molecule, restricting vibration about the glycosidic linkage.

It was anticipated that in both of the structures studied there would be two chemically identical, but crystallographically unrelated, sugar residues. It was therefore hoped that a comparison of the geometry of the two residues would provide not merely a set of average values, but also give some idea of the extent to which different crystal packing might affect the geometry of the residue. It was also hoped that comparison of two different compounds containing the same linkage might indicate how sensitive the conformation of the linkage is to crystal packing.

(b) Trehalose and its Derivatives.

The D-glucosyl D-glucosides are collectively known as the trehaloses. There are three reviews of these compounds in the literature (K. Myrbäck, 1949; M. Hayashibe and K. Aso, 1959; G. Birch, 1964). There are three isomers which have α,α α,β and β,β linkages; all three have been synthesised, but only the isomer with the α,α linkage occurs naturally. It alone is alternatively known as mycose or mushroom sugar. It is widespread in nature where it is found in fungi, bacteria, the blood of insects, algae lichens and some higher plants. It constitutes up to 15% of mushrooms and dried yeast, but more basic foodstuffs apparently contain none, so that it does not constitute an important part of the human diet. The lipids of the human tubercle bacilli, and those in corynebacterium diptheriae, contain esters of α,α-trehalose.

It has been shown that α,α-trehalose yields only glucose on complete hydrolysis (C. Böhning, 1888). From the time of its discovery (H. Wiggers, 1832) it was known to be non-reducing, so that the positions of the glucosyl linkages were necessarily 1,1'. The molecular weight was found to be 350 by the freezing point depression method (L. Maquenne, 1891), so that the molecular formula must be $C_{12}H_{22}O_{11}$. On oxidation with sodium metaperiodate, and with periodic acid, one mole of α,α-trehalose reacted with four moles of oxidant and gave off two moles of formic acid, showing that both rings are pyranoid (E. L. Jackson and C. S. Hudson, 1939; S. Akiya, S. Okui and S. Suzuki, 1952). Similar results were obtained using lead tetra-acetate (R. C. Hockett, M. T. Dienes and H. E. Ramsden, 1943). Methylation followed by hydrolysis was found to yield two moles of 2,3,4,6 tetra-O-methyl-D-glucose (H. Schlubach and K. Maurer, 1925),

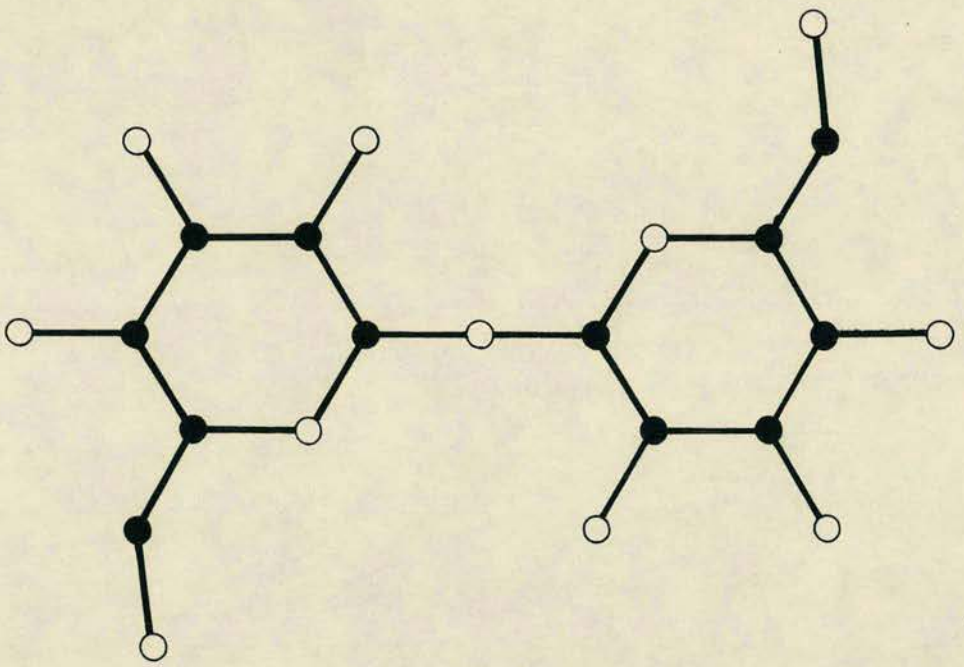
which again showed that the rings were both pyranoid. Thus all the chemical evidence showed that α,α-trehalose consists of two pyranoid rings linked 1,1', as shown (fig 1).

Whereas α,α-trehalose is very soluble in water and in aqueous ethanol, it is nearly insoluble in absolute ethanol. It may be crystallised in an anhydrous form by dissolving crystals of the hydrate in pyridine and distilling the solution at atmospheric pressure in order to remove the water of crystallisation (G. Birch, 1965). From aqueous ethanol it invariably crystallises as the dihydrate. These crystals have been examined by optical crystallography (P. Groth, 1910) and found to be rhombic bisphenoids, with a : b : c = 0.6814 : 1 : 0.4171.

It has been shown that the specific rotations of the three isomers of trehalose and their octa-acetates do not agree with Hudson's rules, although better agreement is obtained with Klyne's rules (J. Staněk, 1957). A further anomaly was discovered when the infra-red spectrum of α,α-trehalose was examined. It has been calculated that the water of crystallisation of carbohydrates should give rise to an absorption at 1645 cm^{-1} (S. A. Barker, E. J. Bourne and D. H. Whiffen, 1956). It was hoped that the determination of the crystal structure might explain the observed pattern of results (G. Birch, 1965):

Maltose monohydrate	1680 cm^{-1} (broad absorption)
Glucose monohydrate	1670 cm^{-1} (broad)
Lactose monohydrate	1660 cm^{-1} (sharp)
Trehalose dihydrate	1690 cm^{-1} (sharp).

α,α- Trehalose.



○ = oxygen

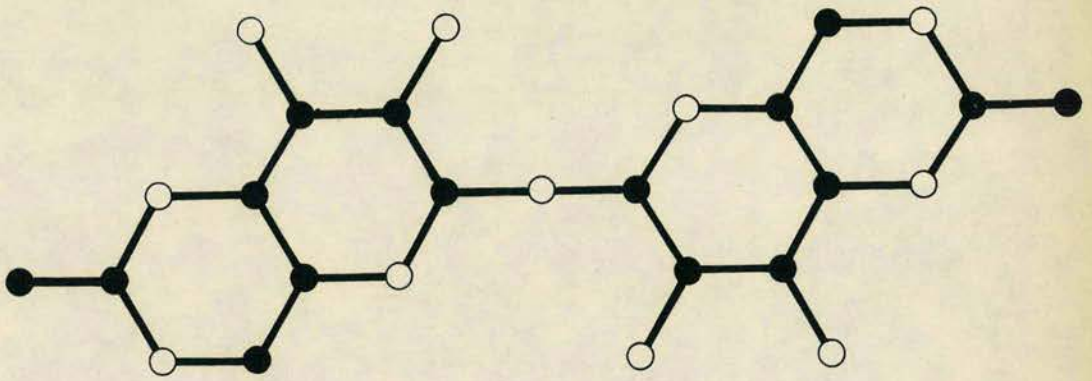
● = carbon

fig (1)

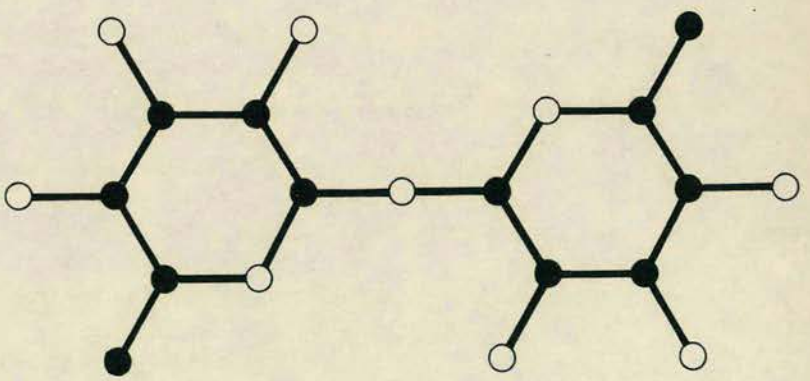
The trehaloses form many crystalline esters and ethers. Crystallisation is favoured by the absence of a free reducing group. There can be no anomeric forms of the products, so that the entropy of a solution is lower than would be the case for a reducing disaccharide. Dr. Birch was kind enough to supply several batches of crystals. These included some large crystals of α,α-trehalose dihydrate which were obtained by several successive recrystallisations from aqueous ethanol. Some anhydrous α,α-trehalose crystals were, unfortunately, far too small for single crystal X-ray diffraction work. There were also crystals of two derivatives, 4,6:4',6'-di-O-ethylidene-α,α-trehalose monohydrate (fig 2) and 6,6'-dideoxy-α,α-trehalose monohydrate (fig 3).

The former compound, referred to henceforth as diethylidene trehalose, was prepared from α,α-trehalose by adding paraldehyde and some sulphuric acid. It was crystallised from 1,4-dioxan-water made alkaline with ammonia. Analysis for carbon and hydrogen, for the acetaldehyde content and for the glucose equivalent were consistent with the formula $C_{16}H_{26}O_{11}$, H_2O. The dideoxy derivative, referred to as dideoxy trehalose, was prepared by hydrogenating hexa-O-acetyl-6,6'-dideoxy-6,6'-di-iodo-α,α-trehalose. The iodine atoms were thus replaced by hydrogen atoms, and the hexa-acetyl-dideoxy compound was then de-acetylated. The product was recrystallised twice from ethanol, but on standing for several days in the mother liquor the crystals redissolved and crystallised in a different form. Analysis for carbon and hydrogen suggested that the crystals were a monohydrate, of formula $C_{12}H_{22}O_9.H_2O$ (G. G. Birch, 1966).

Diethylidene Trehalose.



Dideoxy Trehalose.



(figs 2&3)

(c) Possible Methods of Solution of the Structures.

The formula units of the compounds under consideration each contained over twenty oxygen and carbon atoms. In consequence, even if the asymmetric unit of the crystal structure contained only one formula unit, the most favourable possibility, the problem would nevertheless be one of moderate difficulty. When the work described in this thesis was commenced, the use of direct methods of phase determination in non-centrosymmetric space groups had not attained its present prominence, and therefore a solution was sought by Patterson methods.

The orientation of a pyranoid ring in the "chair" form can readily be deduced from a three-dimensional Patterson synthesis, making use of the characteristic set of multiple-weight vectors which appear close to the origin (C. A. Beevers and T. R. R. McDonald, 1950; C. A. Beevers, T. R. R. McDonald, J. H. Robertson and F. Stern, 1952 inter alia). The presence of ring substituents in equatorial positions increases the potency of this method, favouring its success with the present set of compounds. The problem now becomes that of locating the pyranoid rings in the unit cell, and resolving the ambiguities of the orientations established. Several possible methods were considered:-

(1) In centrosymmetric projections, e.g. projections down two-fold screw axes, there is an accumulation of vectors corresponding to the vector between the centre of one ring and the centre of a symmetry-related ring. This method was applied successfully in the case of glucose (C. A. Beevers and T. R. R. McDonald, 1950), where the centre-centre peak showed up very clearly. For a glucose ring this

vector should be weighted up eight times.

(2) The Harker section (D. Harker, 1936) of the three dimensional Patterson map should contain a complete representation of the molecule. If the orientation of one ring is known then it might be possible to locate it in this way, although past results are not encouraging (C. J. Brown, 1966). It is, however, a quick method to apply, and the Harker sections or section may be used to check trial structures obtained by other methods.

(3) Trial and error methods based on the very strongest intensities have been used successfully for cellobiose (C. J. Brown, 1966), but this method cannot be expected to apply widely. Of course, the strongest intensities must not be ignored, for they do contain information about the structure.

(4) An image-seeking function may be employed, such as the sum function and the theoretically superior minimum function (M. J. Buerger, 1959). This approach is identical to the vector convergence method (C. A. Beevers and J. H. Robertson, 1950).

(5) For any centrosymmetric projection, the triple product sign relationship (D. M. Sayre, 1952) could be employed. This method is not really sufficiently powerful, although the structure of β-D-glucose has been solved in this way (W. G. Ferrier, 1963) using the method of coincidences (D. F. Grant, R. G. Howells and D. Rogers, 1957).

In the field of structure determination, the major change which has taken place in the last few years is undoubtedly the development of the direct methods of phase determination for non-centrosymmetric space

groups. The first structure to be published which had been solved in this way was L-arginine, for which the method of symbolic addition was used (I. L. Karle and J. Karle, 1964). This technique was described in detail in a later publication (J. Karle and I. L. Karle, 1966). It soon became apparent that this was a powerful method, capable of solving intricate structures and of extending and refining partial solutions.

Patterson methods indubitably work best for "heavy atom" compounds, and are least effective for compounds which are composed entirely of light atoms. The phase relationships used in the direct approach were originally deduced using the simplifying assumption that all the atoms in a structure are equal in magnitude. It is therefore to be expected that direct methods will be superior to Patterson methods of solving light atom structures. It has been found that the presence of heavy atoms does increase the ease of finding the correct solution using the Sayre sign relationship, so it might be expected that the presence of heavy atoms in a non-centrosymmetric space group would also facilitate the phase determination.

Two possible advantages of direct methods compared to Patterson methods are also relevant. In the first place, it is quite possible to obtain an erroneous solution of the Patterson summation and think it correct; using direct methods the distinction between success and failure is often more obvious. Secondly, assuming that a correct solution is obtained by both methods, that obtained by phase relationships is likely to refine much more rapidly. This is because the errors in the parameters deduced by direct methods are likely to be small and randomly distributed,

whereas those in a Patterson solution are likely to be larger and to be, at least partly, systematic.

It was not, however, at any time the object of the candidate to make a rigorous comparison of the merits of these two methods, but rather to find the best method available for the solution of saccharide structures. It seems clear that the two methods can complement each other, and, specifically, that the Patterson summations can be used to help interpret a map obtained by direct methods, and to indicate the plausibility of a trial structure. For these purposes the ring orientations deduced from the Patterson summations may be employed. The data necessary are the same for both methods, i.e. a set of accurate intensity data, and accurate cell dimensions to carry out the appropriate corrections. It is probable that the use of inaccurate data will be more prejudicial to the chance of success using phase relationships than to that using Patterson methods.

Although there have been considerable changes of emphasis in the field of crystallography since the work recorded in this thesis was commenced in 1965, nevertheless the objectives of the work have not changed. They were firstly to solve the structures of some disaccharides, thereby obtaining useful stereochemical information about the molecules themselves, and secondly, to examine the methods of solving such structures. That the second of these aims has been overtaken by events is, of course, a cause of rejoicing.

SECTION I: α,α-TREHALOSE DIHYDRATE

1. PRELIMINARY INVESTIGATION

(a) The Apparatus Used.

A normal-beam vertical travel Weissenberg camera of 10 cm diameter was used with a Newton-Raymax self-rectifying X-ray tube. It was run at 50,000 V and 20 mA with a copper target and, sometimes, a nickel filter to remove the Cu K_β radiation. This instrument was used to determine the space group and the accurate unit cell dimensions. A Unicam horizontal travel equi-inclination Weissenberg camera of 5.73 cm diameter was used with a Philips P1010 generator, which was run at 40,000 V and 20 mA with a copper target and a nickel filter. This was used to obtain the photographs from which the intensity data were measured. A Philips PW 1051 powder diffractometer was also used with the above generator. All X-ray exposures were carried out at about 18°C. Ilford "Industrial G" film was used on all occasions. It was developed at about 18°C for five minutes in PhenX developer, and was then fixed for twice the clearing time.

(b) Physical Examination.

Crystals of α,α-trehalose dihydrate are described as rhombic bisphenoids with a : b : c = 0.6814 : 1 : 0.4171. The commonly observed faces are (120), (110), (101), (011) and (111), and occasionally found are (100) and (010). There is a cleavage plane parallel to (110). The crystals are optically biaxial, with 2V = 50°16', 2E = 78°56' and β = 1.478, all referred to Na D light (P. Groth, 1910). Very good

crystals were supplied by Dr. Birch. They were colourless, and showed very clear extinctions when viewed between crossed polarisers. The largest crystals showed a feeble piezo-electric effect, suggesting that they belong to a non-centrosymmetric space group. This was necessarily so, since the material was known to consist of only one stereo-isomer. It was noted that the crystals had a cleavage plane, and when some of the batch were split up into fragments this was identified as parallel to (110) as Groth reported.

The density was known to be about 1.52 $g.cm^{-3}$ (G. G. Birch, 1965a). Small fragments of a good large crystal were found to have a density of 1.512 $g.cm^{-3}$ by the method of flotation. The two liquids used, carbon tetrachloride and toluene, were very close to the value sought, which increased the accuracy of the method.

(c) Space Group Determination.

Specimens were used which were elongated parallel to the axis of rotation, which was arranged to coincide with an axial direction. Oscillation photographs were used in order to adjust the orientation so that the axis of rotation was accurately parallel to the axial direction of the crystal. Weissenberg photographs of the zeroth and first layers were then obtained, using a 200^{o} oscillation. The diffraction patterns were all symmetrical about the zero layers, showing that the symmetry of the crystals is orthorhombic. The only systematically absent reflections were:

I(h00) when h was odd;

I(0k0) when k was odd;

I(00ℓ) when ℓ was odd.

This information is only consistent with one space group, $P2_12_12_1$, which

is number 19 (International Tables, vol I). From the oscillation photographs a, b and c were found to be 12.2, 17.9 and 7.6 Å respectively. It was calculated thence that the number of molecules in the unit cell was four, equal to the number of equivalent positions in the space group, so that the asymmetric unit of the structure contains one molecule.

(d) Accurate Cell Dimensions.

Zero layer Weissenberg photographs were used, which were calibrated by the sharp shadows of brass knife-edges at accurately known angles of about $\theta = 84.5^{\circ}$. The angles of these knife-edges were checked firstly by physical measurement of the instrument and secondly by using a sample of pure rock salt as a standard. The wavelengths of the radiation used were taken to be 1.5405 and 1.5443 Å for Cu K_{α_1} and K_{α_2} respectively. The cell parameter of the rock salt was calculated to be 5.639 Å, compared to the accepted value of 5.640 Å (International Tables, vol III), the difference being within the errors of measurement of the film. The film used for measurement was of recent origin, since it was found that films tended to become distorted over a period of time. All equivalent spots on the film were measured separately and then an average value was taken. Only spots close to the knife-edges were used to obtain values of θ.

In the calculations an extrapolation to $\sin^2\theta = 1$ was used in order to minimise the errors due to absorption by the crystal, eccentricity of the specimen, et cetera (A. J. Bradley and A. H. Jay, 1932 a and b). It also has the effect of reducing any error due to incorrect values for the angles of the knife-edges. A value for one of the reciprocal cell dimensions, say a*, was assumed and substituted into the expression:

$$4.\sin^2\theta = h^2.a^{*2} + k^2.b^{*2},$$

where $a^* = \lambda/a$, etc.

Thus a series of values of b* were calculated, the more accurate being for those reflections with low h. This value of b* was now used to generate a value of a*, and then the process was repeated. The values thus obtained were much more accurate than the starting ones, which depended on measurements of oscillation photographs. The value of a*/b* was now used to plot a graph of b* against $\sin^2\theta$. The points on this graph were examined to see how closely they fitted a straight line, and to see if there were a correlation between deviations from the line and the indices of the reflections concerned. Any such correlation indicated that the value of a*/b* was inaccurate. This ratio was varied to get the best simultaneous fit of graphs of a* and b* against $\sin^2\theta$. Finally, the values obtained by the extrapolation of these two graphs were found to yield the same ratio of a*/b* as that used to generate them, indicating that this refinement process had terminated.

Estimates of the accuracy of the results were made by considering the spread of the points on the graph, and, where there were more than ten independent reflections used, calculating values and a standard deviation from the simplified least squares formula:

$$\bar{y} = \bar{m}.\bar{x} + \bar{c} \; ; \qquad \bar{m} = \frac{\sum X_i.Y_i}{\sum X_i^2} \; ,$$

where $\bar{m}$ = gradient of the best straight line,
$\bar{x}, \bar{y}$ = mean value of the variables,
$\bar{c}$ = intercept of the best straight line,
X_i, Y_i = difference between each value of a variable and its mean.

This formula assumes that the relative accuracy of one of the variables is much greater than that of the other. Here, the relative accuracy of the reciprocal dimensions is very poor, despite the fair absolute accuracy; the $\sin^2\theta$ values are relatively more accurate, though absolutely less so.

The results obtained, and three times their estimated standard deviations, are:

$$a = 12.233 \pm 0.009 \text{ Å}$$
$$b = 17.889 \pm 0.013$$
$$c = 7.596 \pm 0.006$$

An attempt was made to check these results using the powder diffractometer, but the intensities obtained were too weak for accurate measurement. It was noted that the powder samples were not stable, the traces obtained changed after even as short a time as a few minutes. This was clearly due to a change in the state of hydration of the material, presumably caused by the crystals absorbing atmospheric water vapour. For single crystal samples it appeared that only a very thin outer layer was affected in this way, but this did suggest that very small single crystals might be unreliable.

From the above cell parameters, assuming that there were two molecules of water of crystallisation per α,α-trehalose molecule, and that $Z = 4$, the density was calculated to be 1.511 $g.cm^{-3}$. This was in fortuitously good agreement with the observed value of 1.512 $g.cm^{-3}$, since the combined errors of observation amounted to far more than 1 in 1,500.

2. THE INTENSITY DATA

(a) The Collection of the Intensity Data.

Accurate absorption corrections can easily be made for crystals which are either spherical or cylindrical, with the restriction that in the latter case the axis of the cylinder must coincide with the axis of rotation of the crystal. Since it was intended that one specimen be used to obtain photographs with the crystal rotating about all three crystallographic axes, it was decided to use a spherical specimen, ground to shape on emery paper (W. L. Bond, 1951). The process of grinding a sphere may break up the internal order of the crystal and thus reduce the effects of secondary extinction.

Although there is no "optimum size" for a spherical crystal, several factors must be considered in deciding the size of the specimen. If the crystal is large the range of absorption corrections will also be large, a source of error, and the crystal may not be totally "immersed" in the X-ray beam. On the other hand, if the crystal is small then longer times will be required for its exposure, and it will be relatively more affected by the thin layer of atypical material on the outside which is due to hydration effects. The linear absorption coefficient of the crystals was found using the equation (M. J. Buerger, 1942, p.181):

$$\mu = G \left\{ P_O \left(\frac{\mu}{\rho}\right)_O + P_H \left(\frac{\mu}{\rho}\right)_H + P_C \left(\frac{\mu}{\rho}\right)_C \right\} ,$$

where μ = linear absorption coefficient,
G = density ($g.cm^{-3}$),
P_O = proportion of oxygen, etc.,
$\left(\frac{\mu}{\rho}\right)_O$ = atomic absorption coefficient of oxygen, etc..

Hence it was found that $\mu = 12.2\ cm^{-1}$. If r = the ratio between the values of the absorption correction at $\theta = 90^{\circ}$ and 0°, then:

μR	r	R
2	2.6	1.64 mm
1	1.37	0.82
0.5	1.09	0.41

A crystal of radius about 0.4 mm was felt to be a good compromise, as it was small enough to be totally immersed in the X-ray beam and any error in the absorption correction would be small.

As the crystals have a pronounced cleavage plane, the application of thermal shock treatment to break up their internal order and so reduce the secondary extinction errors did not seem wise. Past experience of saccharide structures suggested that these errors were likely to be very small, so it was hoped that the shock necessarily experienced by the crystal in the grinding process would prove adequate for this purpose.

Grinding a suitable specimen was made difficult by the cleavage plane. Prolonged gentle grinding of roughly cubical segments yielded products which were pronouncedly elliptical. It was found that grinding for only five minutes at a faster rate gave either a good approximation to a sphere, or, more frequently, a fine powder. When a suitable crystal was obtained it had to be mounted at random and then adjusted to the desired orientation by means of oscillation photographs. The first sphere to be photographed broke in half overnight, when the X-ray generator and the camera were both switched off! This happened when the crystal was being orientated. A second sphere fractured at a similar stage.

A third sphere, very slightly elongated, had mean radius = 0.3 mm. It was successfully mounted on the equi-inclination camera and aligned to rotate about its z axis. Equi-inclination Weissenberg photographs were taken of the layers $l = 0$ to $l = 5$, then the crystal was re-oriented about the crystallographic y axis and photographs were obtained of the layers $k = 0$ and $k = 1$. At this point this crystal cracked so a fourth sphere was now ground. It had a mean radius of 0.37 mm and was closely spherical. It was used for photographs up the y axis, for $k = 0$ to $k = 14$, and the x axis, for $h = 0$ to $h = 9$. The maximum equi-inclination angle attained was about 36°, the practical limit on the camera used. The equi-inclination angles were calculated from the expression:

$$\sin\mu_e = \frac{3}{2} \quad , \qquad \text{where } \mu_e = \text{equi-inclination angle,}$$
$$3 = \text{reciprocal lattice height.}$$

They were checked from a chart (M. J. Buerger, 1942, p.294) and the Weissenberg screen settings were found from a graph (ibid., p.295). For each layer a test strip was exposed, to ensure that no spots would be cut off accidentally by the screens.

Photographs were taken using multiple packs of three films. Fresh developer was made up fairly frequently. For each layer two exposures were made, one of seven hours and the other of twenty-five minutes, which corresponded to two complete oscillations through the 197° range used. The X-ray generator was run continuously for the shorter exposure and the shutter was opened and closed manually as the camera reversed at the end of a traverse.

An intensity strip was prepared for both the crystals used. This was done by using the Weissenberg screens to expose only a very small portion of film at a time, and recording a 5^{o} oscillation photograph. Successive portions of the film received increasing exposures of from 1 up to 60 oscillations. For all except the lower end of the scale the increase in exposure from one strip to the next was between 7 and 10%. A low angle reflection, forming a circular spot, which was barely discernible on the weakest strip was chosen as the foundation of the scale, and the rest of the film was masked off. The object of the intensity strip was to allow for any non-linearity in the response of the film.

The intensities of those spots on each film which fell within the range of the intensity strip were now measured. As the eye is an efficient integrator, allowance for spot shape variation was incorporated into the measurements as they were made. The large spot size, and the approximately circular spot shape facilitated this. Indeed, trials suggested that it would be very difficult to avoid making some correction to the intensities in this fashion, so that the application of a theoretical spot shape correction would probably have produced inferior results. The only serious errors arose for spots close to the middle of films taken at high μ_e angles. In these cases both the extended and contracted forms of the reflection were measured and their harmonic mean taken to be correct. In the case of the highest order reflections complete separation of the reflection into its α_1 and α_2 components occurred and it was found that the most accurate procedure was to measure only the α_1 component and then add 50% to the measured value.

In some zero layer photographs very weak spots were noticed in positions forbidden by the space group extinctions. These were identified as Renninger reflections, due to multiple diffraction. (They were almost certainly due to double diffraction, otherwise they would have been too weak to observe.) This identification was based on (a) the spots were very small because of the extremely demanding geometry of multiple diffraction; (b) they varied in intensity when photographs were taken about different axes; (c) they disappeared when the crystal was set very slightly off the axis. Since all these spots were very weak, it was assumed that double diffraction would not have a significant effect on any of the measured intensities. It could only be important in the case of a weak spot, and then the peculiar intensity profile of the spot would be sure to attract attention.

(b) The Correction and Scaling of the Intensity Data.

The data collected were readily scaled in individual layers. The ratio of intensities between two adjacent films from a pack lay in the range 2.9 to 3.0. The precise value of this factor was always found experimentally, for which purpose it was necessary to weight down the values at both the top and the bottom of the scale of the intensity strip. Lorentz, polarisation and absorption corrections were applied simultaneously using a program written by Dr. Harding for the KDF9 computer.

The sets of intensity data from the two different spheres were now treated separately. Both sets of data were scaled in the usual way, using those spots which were measured twice, about two different axes. The very weak, the very strong, the very low angle and the high angle reflections

were weighted down as they were likely to be less accurate. Investigation revealed that this weighting had little effect on the ratios obtained, which was just as well since for some of the higher layer films these conditions had to be relaxed in order to obtain a reasonable number of common reflections. The two sets of data were scaled together in the same way. The final value of each intensity was taken to be the arithmetic mean of all the separate scaled values.

In all there were approximately 5,500 measurements which gave a total of 2,097 observed reflections and 52 non-systematic absences, i.e. 2,149 independent reflections. The number of reflections, excluding systematic absences, which were accessible with copper radiation was calculated to be approximately 2,172. Thus intensities were measured for 98.9% of the theoretically accessible reflections, although some of these were estimated to be zero.

The standard deviation of an observed structure factor which has been measured twice can be estimated (J. A. Ibers, 1956) according to the equation:

$$\sigma(F_0) = 0.89 \left| |F_1| - |F_2| \right| ,$$

where $|F_1|$ and $|F_2|$ are the two observed values.

Values calculated from this equation give an idea of the accuracy of the observed data. It was found that the bulk of the observed $|F_0|$ data had a standard deviation of about 5%, but that the very weakest and strongest intensities led to considerably worse values (Table 1). These results also indicate the accuracy to be expected in the final refinement of the correct structure.

TABLE 1

The Accuracy of the α,α-trehalose Intensity Data.

Range of I	ND	$\sigma(F)$
1 - 9	305	30.6%
10 - 29	934	15.4
30 - 59	809	9.0
60 - 99	694	7.2
100 - 199	868	5.6
200 - 299	440	5.2
300 - 399	254	5.4
400 - 499	160	5.2
500 - 599	143	4.6
600 - 799	183	5.6
800 - 999	121	4.8
1000 - 1999	185	5.2
2000 - 2999	126	5.2
3000 - 4999	48	8.4
$\geq$ 5000	29	9.4
TOTAL	5299	9.4

ND represents the number of duplicated measurements.

(c) Intensity Statistics.

We can express the observed intensity, I_{obs}, in terms of the unknown atomic positions, x_n, y_n and z_n, where f_n is the atomic scattering factor of the n^{th} atom, as follows:

$$I_{obs} = K.\left\{\sum_{n=1}^{N} f_n.\exp 2\pi i(hx_n+ky_n+\ell z_n)\right\}^2.\exp(-2B.\sin^2\theta/\lambda^2)$$

The summation is over all the N atoms in the unit cell, and B represents the mean temperature factor for all the atoms. The corresponding structure factor, F_{obs}, is given by the expression:

$$F_{obs} = \sqrt{K}.\sum_{n=1}^{N} f_n.\exp 2\pi i(hx_n+ky_n+\ell z_n) \;.\; \exp(-B.\sin^2\theta/\lambda^2)$$

In order to find the mean temperature factor, B, for all the atoms in the unit cell and the scale factor required to convert the data to the absolute scale, the usual method was employed (A. J. C. Wilson, 1942). A program was available to perform this calculation on the Atlas computer.

All the intensities, excluding only those which were systematically absent, were used. The program resolved the data into twenty equal ranges of $\sin^2\theta$ and worked out the mean $|F_{obs}|^2$ and the mean $\sum f_n^2$ for each range. Only the oxygen and carbon atoms were considered, as the hydrogen atoms make little contribution to the intensities of low order reflections and almost none to those of high orders.

$$\text{As } \sin^2\theta \rightarrow 0 \qquad \ln\left(\frac{\overline{|F_{obs}|^2}}{\sum f_n^2}\right) \longrightarrow \ln K$$

Generally, $$\ln\left(\frac{\overline{|F_{obs}|^2}}{\sum f_n^2}\right) = \ln K - 2B.\sin^2\theta/\lambda^2$$

Hence if a graph of $\ln\left(\frac{\overline{|F_{obs}|^2}}{\sum f_n^2}\right)$ is plotted against $\sin^2\theta$, K may be evaluated from the intercept and B from the slope.

The graph obtained for α,α-trehalose was not a straight line but was perturbed, presumably due to the fact that instead of the assumed random distribution of atoms, they are instead very frequently 1.5 or 2.5 Å removed from other atoms. The results obtained were K = 0.87 and B = 2.3 $Å^2$. The mean thermal parameter was thus comparable in magnitude to the corresponding values for other sugar structures.

The program also plotted the N(Z) distribution (E. R. Howells, D. C. Phillips and D. Rogers, 1950) for all the data and separately for the (0kℓ), (h0ℓ) and (hk0) sets of projection data. The results are shown below (Table 2), comparing the fractions, N(Z), of reflections whose intensities are equal to, or less than, a fraction Z of the average intensity. These results show that the three projections are all centrosymmetric, whereas the data as a whole belong to a non-centrosymmetric space group. This was a confirmation that the space group was assigned correctly.

TABLE 2

The N(z) Test for α,α-trehalose.

	Theoretical		Observed N(Z)			
Z	Centro	Non	(hkℓ)	(0kℓ)	(h0ℓ)	(hk0)
0.1	0.25	0.10	0.08	0.18	0.17	0.18
0.2	0.34	0.18	0.17	0.26	0.28	0.28
0.3	0.42	0.26	0.26	0.32	0.38	0.38
0.4	0.47	0.33	0.33	0.37	0.44	0.45
0.5	0.52	0.39	0.40	0.43	0.49	0.52
0.6	0.56	0.45	0.47	0.49	0.53	0.58
0.7	0.60	0.50	0.52	0.58	0.58	0.62
0.8	0.63	0.55	0.56	0.63	0.60	0.67
0.9	0.66	0.59	0.61	0.67	0.62	0.69
1.0	0.68	0.63	0.65	0.69	0.69	0.71

3. THE PATTERSON APPROACH

(a) Preliminary Discussion.

Before any Patterson summation is calculated, consideration must be given to the possibility of modifying the Fourier coefficients. ~~There is nothing sacrosanct about the observed intensities, since the~~ The observed mean temperature factor to some extant depends on the precise conditions of crystal growth, while the form factors depend on the distances between electrons and the nucleus. Both these factors are, as far as the would-be solver of a structure is concerned, quite arbitrary. The observed data without any modification will be dominated by the low angle reflections, so that a map will suffer from poor resolution, but on the other hand the effect of any sharpening must be considered carefully.

It is not always helpful to sharpen a Patterson map to such an extent as the "point atom at rest" approximation, in which the fall-off due to thermal vibration and the form factor contribution are both eliminated. The very high order reflections, which are measured less accurately, would then be weighted as heavily as all the other data. The use of a small portion of the infinite reciprocal lattice, with a sharp cut-off limit, would give rise to serious series termination effects. This effect could, of course, be reduced by using radiation of shorter wavelength to sample a larger volume of reciprocal space, at the cost of much extra labour. In short, the sharper a Patterson map becomes, the more detail it contains, but the extra detail may be spurious.

As a compromise, a modest amount of sharpening was utilised for α,α-trehalose. The peaks initially sought were of multiple weight.

These peaks were unlikely to be lost in spurious background due to sharpening and it was thought that in the absence of any sharpening they might be too diffuse for accurate measurement. In any case the worst "diffraction ripples" were expected close to the origin of the map, so since the peaks closest to the origin are multiple weight peaks 1.5 and 2.5 Å distant from it no such difficulties were anticipated.

In applying sharpening to the observed intensities full allowance was made for the thermal motion of the atoms using $B = 2.3$ Å^2 as found from the Wilson plot. For the form factor contribution the hydrogen atoms were ignored and the nitrogen curve was taken as a reasonable approximation to the appropriate function of the carbon and oxygen curves. The function $\left\{(7 + f_N) / 2\right\}^2$ was used instead of f_N^2. This had the effect of reducing the weight of intensities as $\theta \rightarrow 90^\circ$. Close to 90° an intensity was weighted down by a factor of six compared to the effect of point atom at rest sharpening.

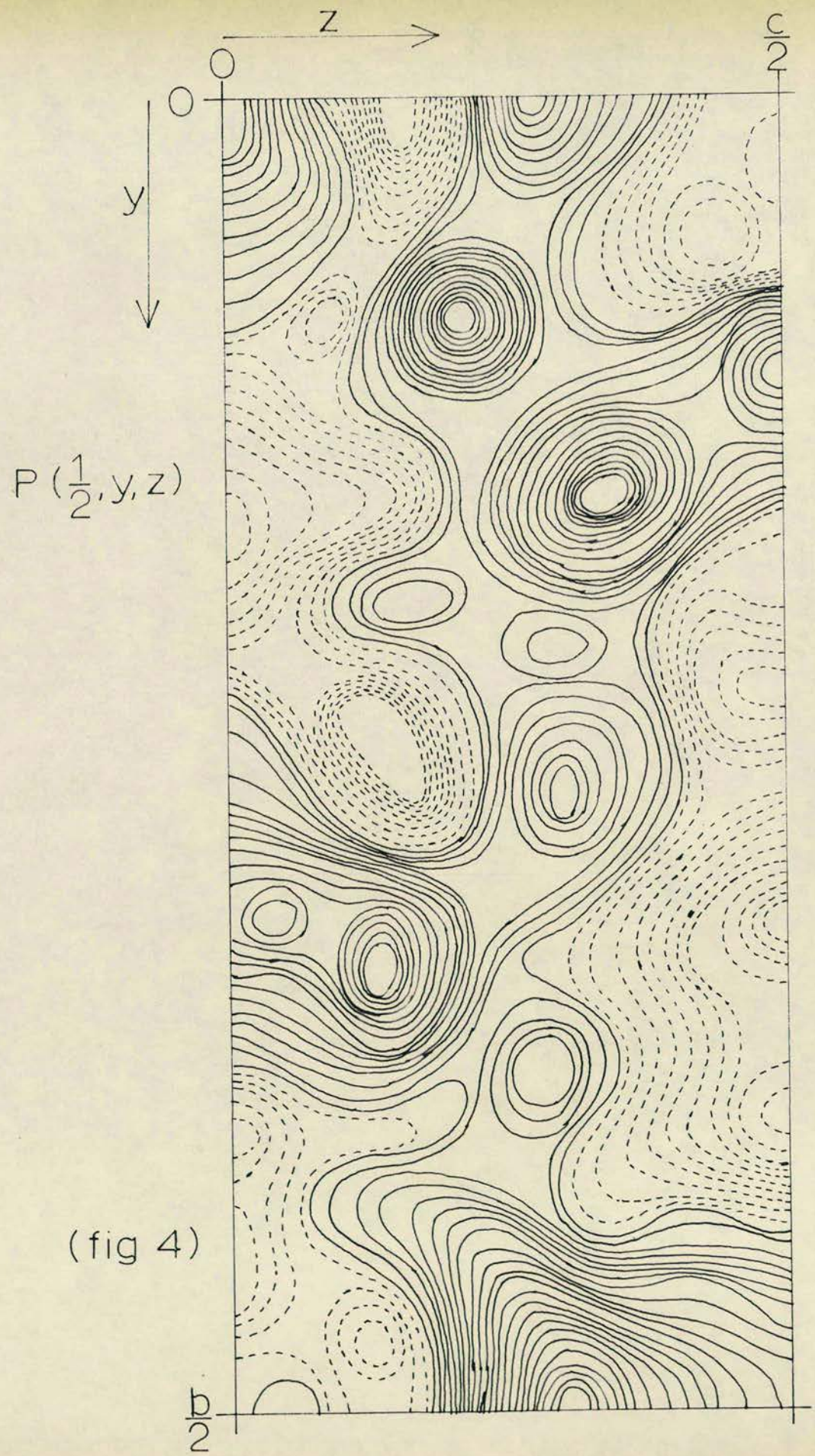
The sharpening of the coefficients and the summation were carried out by the Atlas computer, using a program made available by Dr. Harding. The Patterson map corresponding to space group $P2_12_12_1$ has symmetry Pmmm, so that the asymmetric unit is one eighth of the unit cell. The summation was therefore from 0 to $\frac{1}{2}$ up each cell edge. The intervals between sections were chosen to be less than 0.3 Å in order not to miss any important detail. At a later time a second three-dimensional Patterson synthesis was computed with less sharpening; only a part of the thermal vibration was allowed for. This map was naturally of much lower resolution than the original one. The three Harker sections from the original map are shown (figs 4, 5 and 6) along with one from the second map (fig 7).

A composite map, obtained by projecting the original three-dimensional synthesis on to (001) is also shown (fig 8).

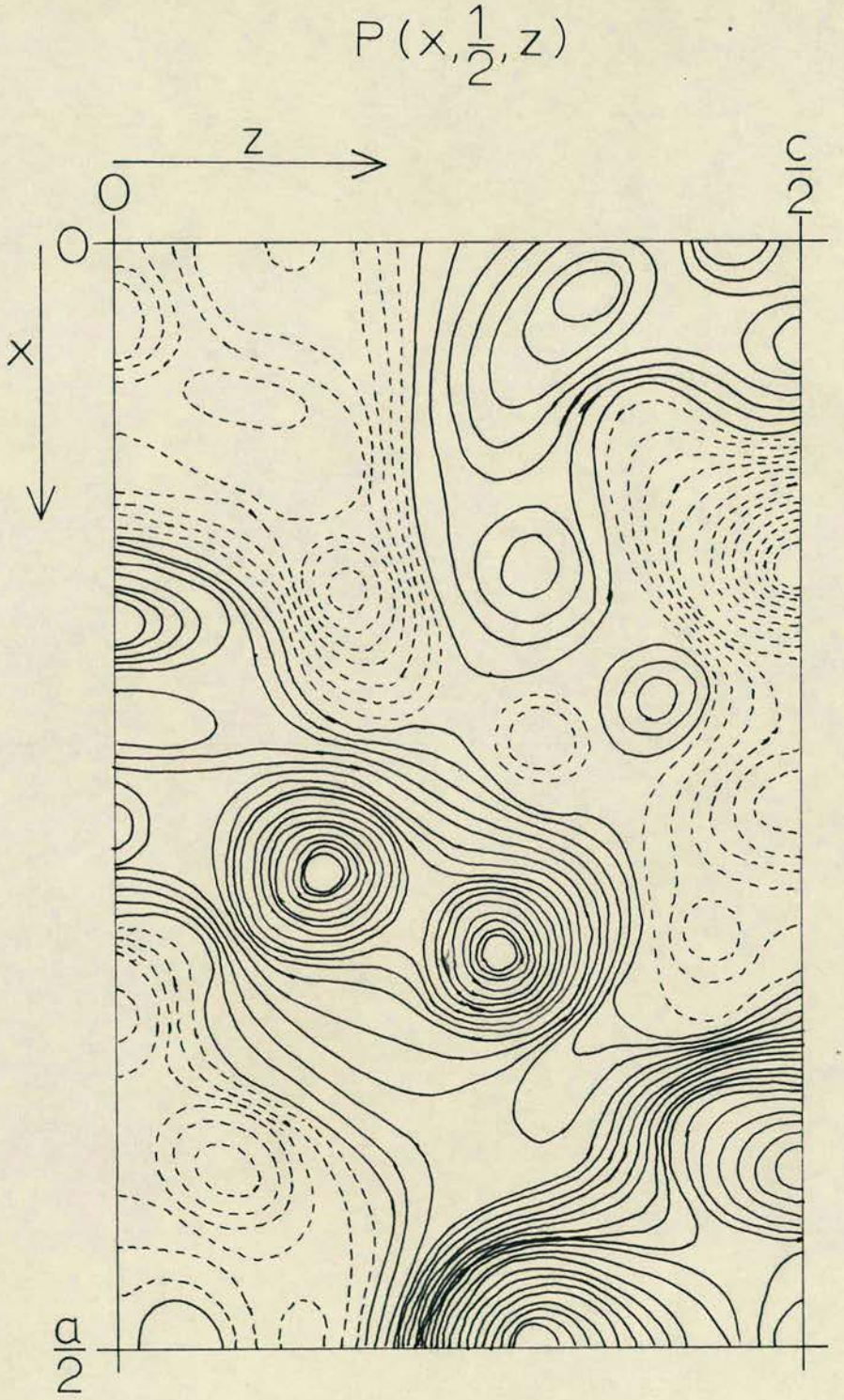
It was obvious that in projection there would be a considerable amount of overlap of vectors so it was decided to compute several maps for each projection. One map for each projection was computed with very little sharpening using the Beevers-Lipson strips (H. Lipson and C. A. Beevers, 1936). Two further maps were computed for each projection using a program written by Dr. Gould; one of these employed point atom at rest sharpening and the other contained only the thermal vibration contribution. The maps calculated by hand were of too low resolution to be of any use, and the projections down the 17.9 Å axis suffered from very considerable overlap. Some of the maps obtained are shown (figs 9 - 13).

(b) The Orientations of the Pyranoid Rings.

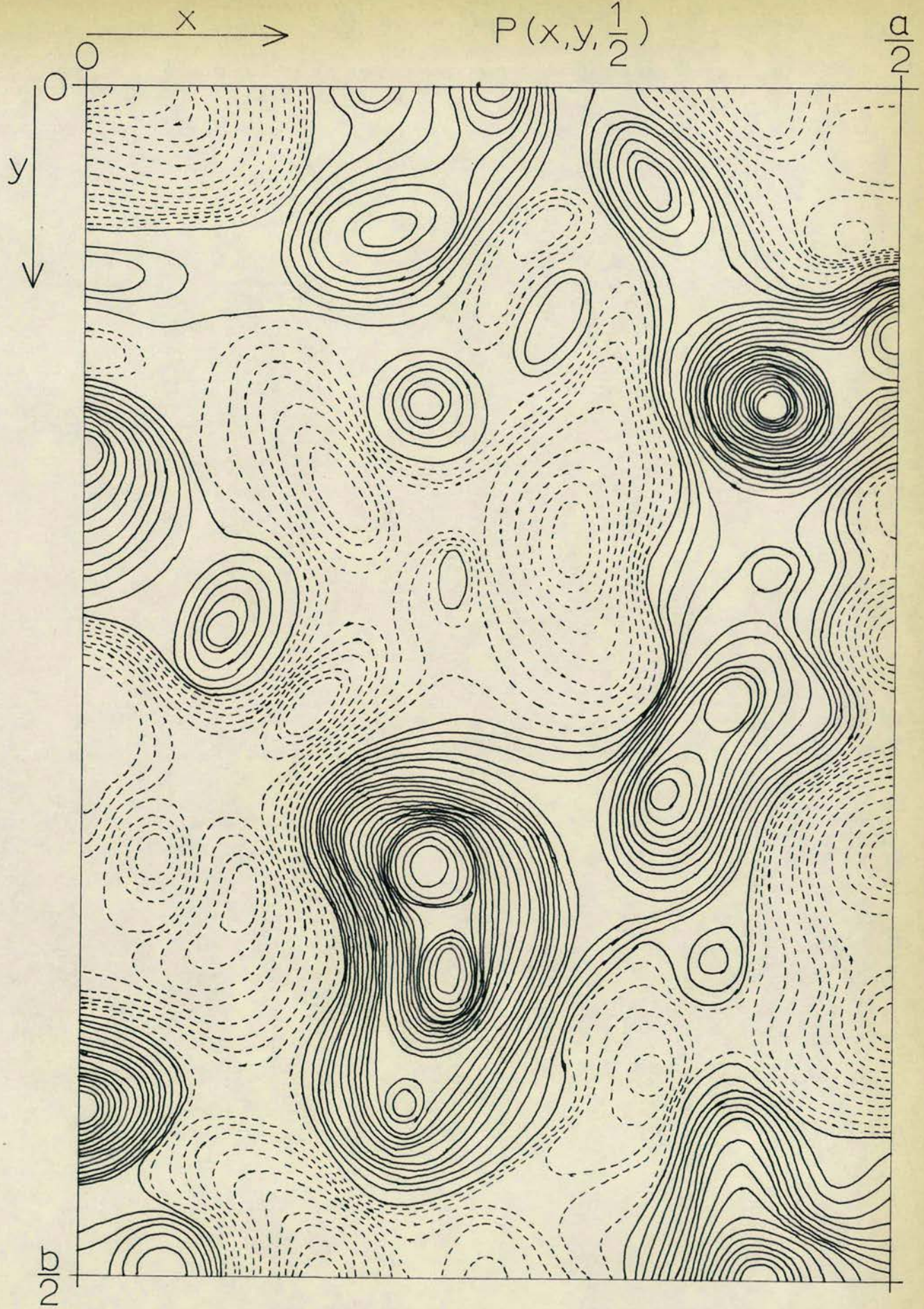
The characteristic set of six 1.5 Å vectors, between atoms bonded together, and six 2.5 Å vectors, between next nearest neighbours, has been used to determine the orientation of a pyranoid ring in a sugar structure on many previous occasions (C. A. Beevers and T. R. R. McDonald, 1950, et seq.). The method used is a very powerful one, as the region of Patterson space which contains the peaks corresponding to these vectors contains very few other peaks, which should be of much lower heights than those sought. In the α,α-trehalose molecule forty out of forty-eight 1.5 Å vectors and fifty-six out of seventy 2.5 Å vectors belong to these sets.



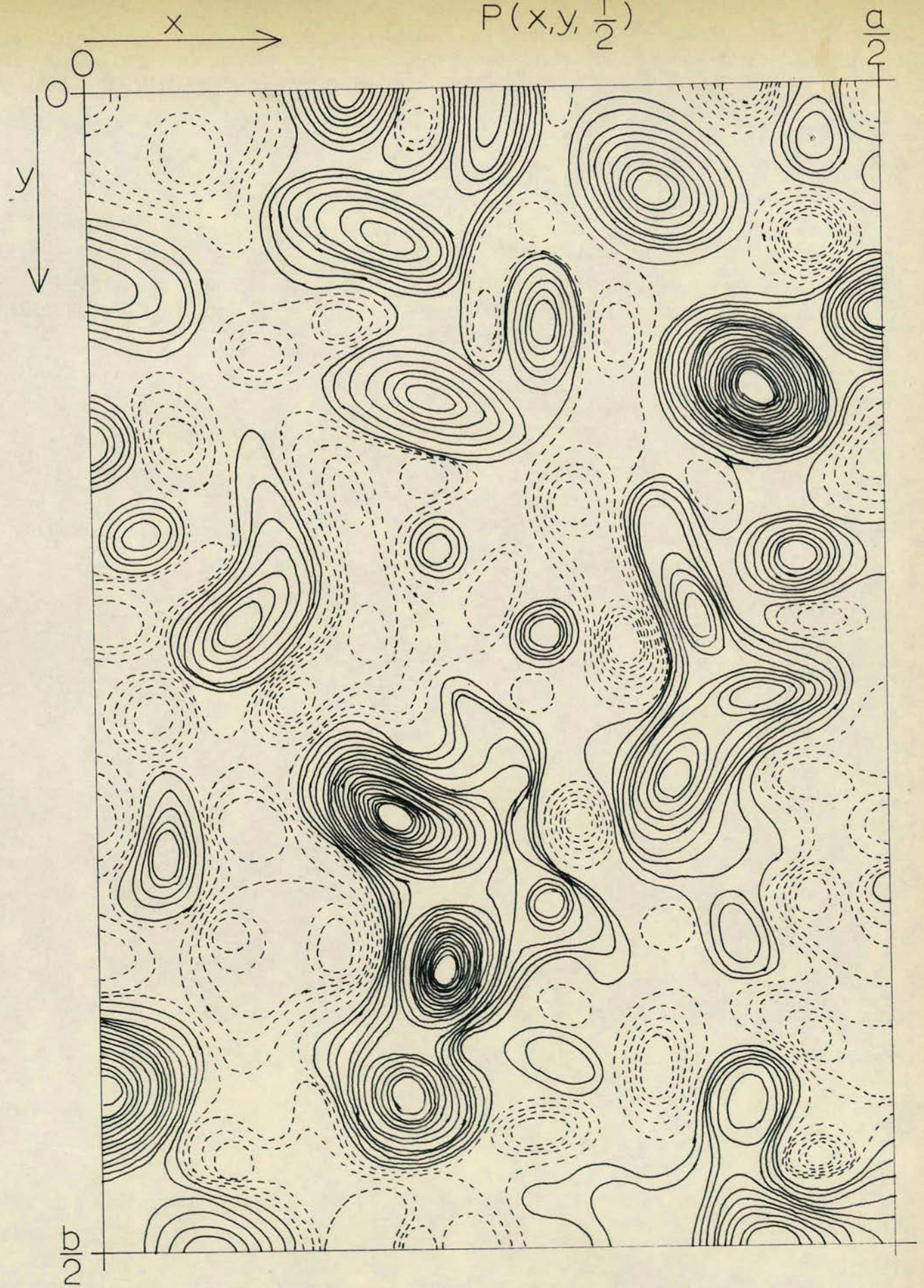
(fig 4)



(fig 5)

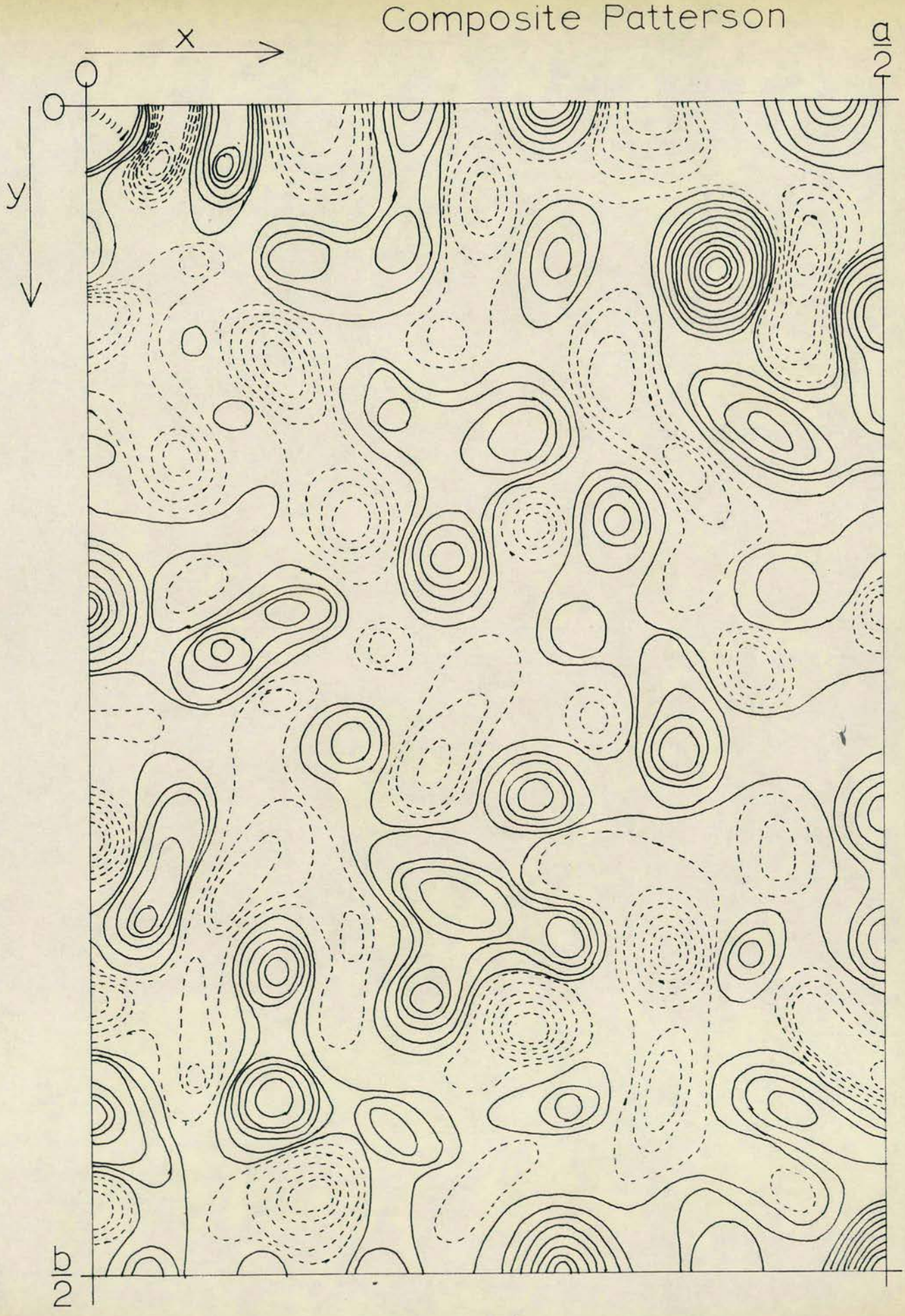


(fig 6)

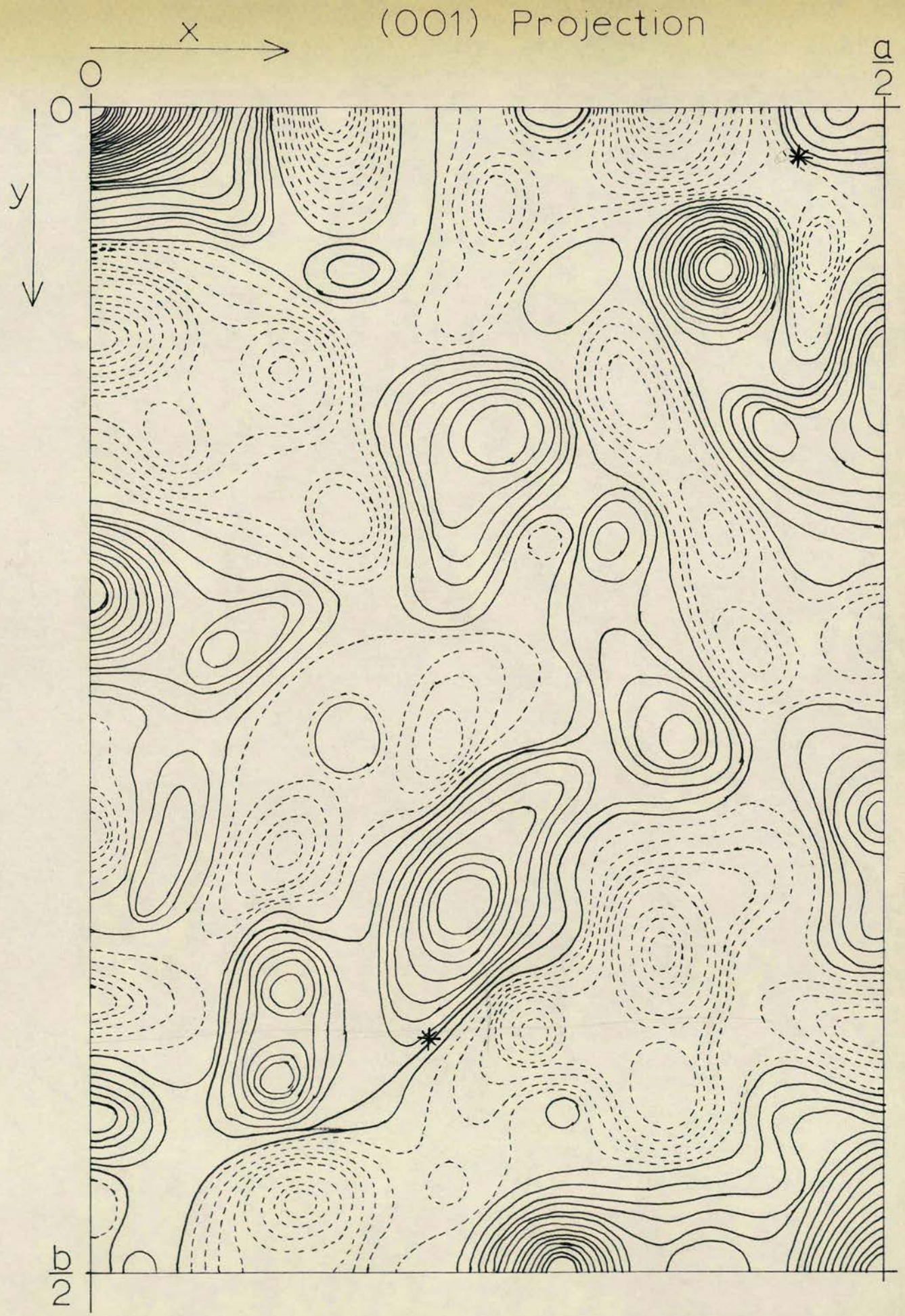


(fig 7)

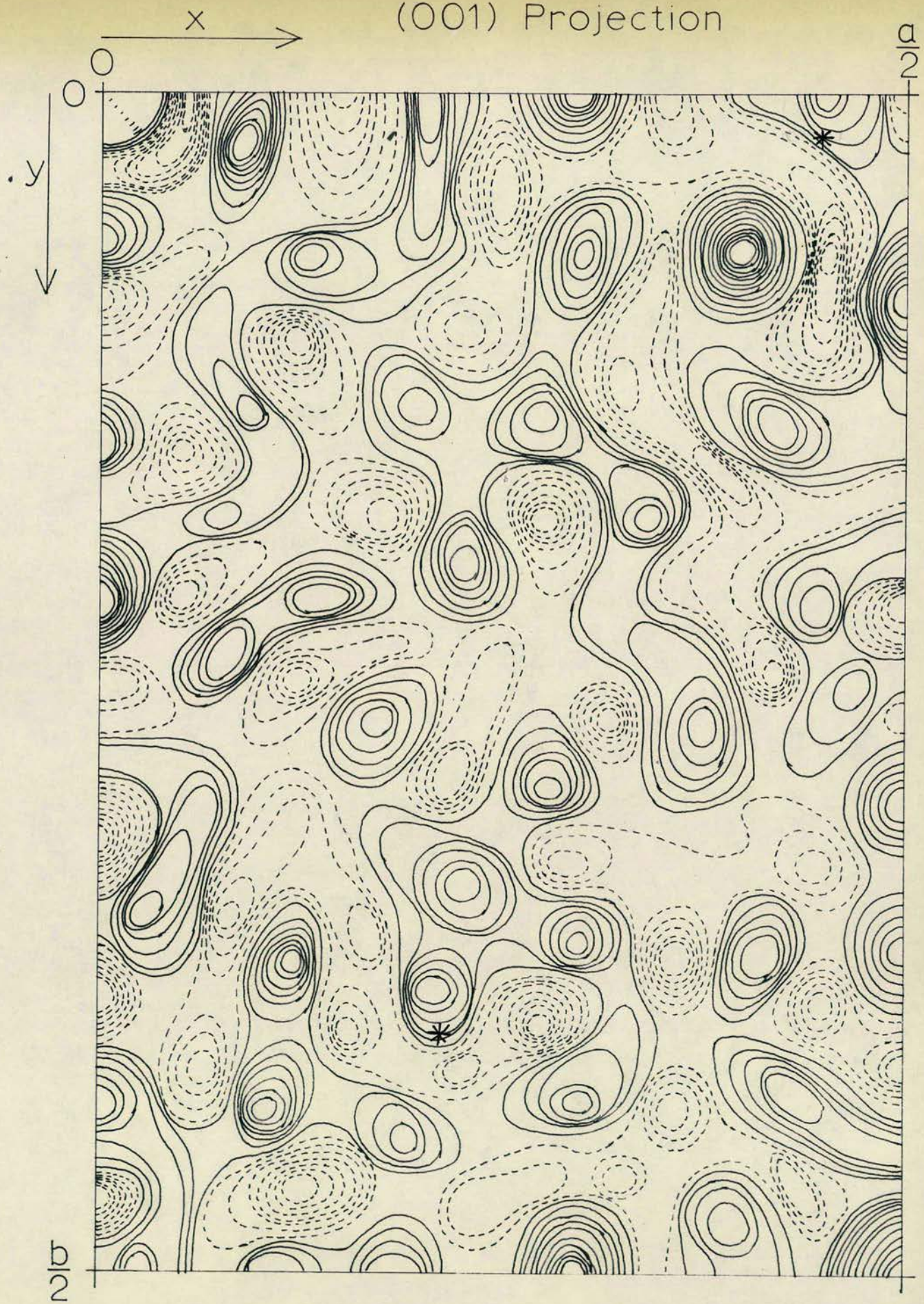
Composite Patterson



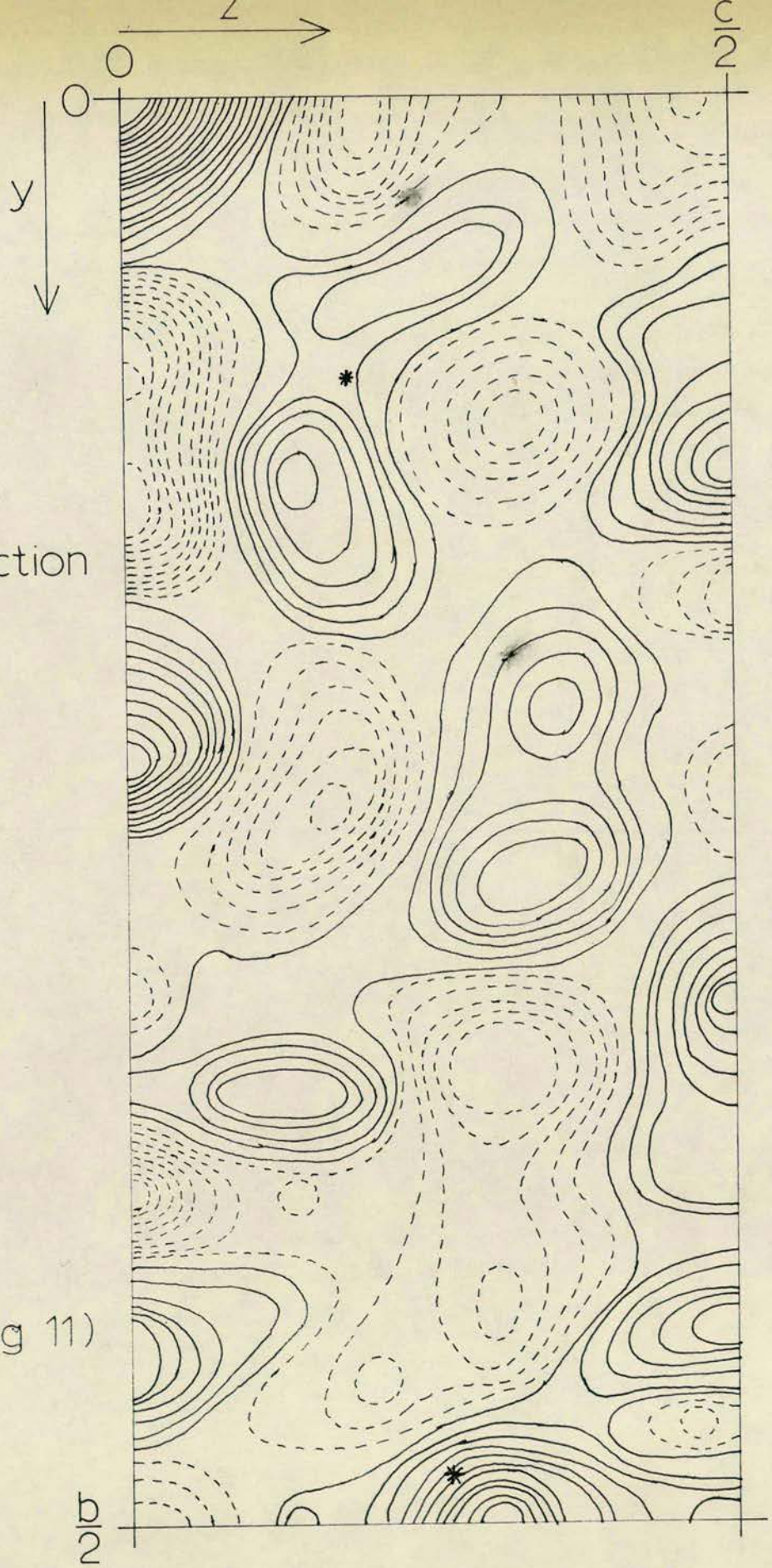
(fig. 8)



(fig 9)

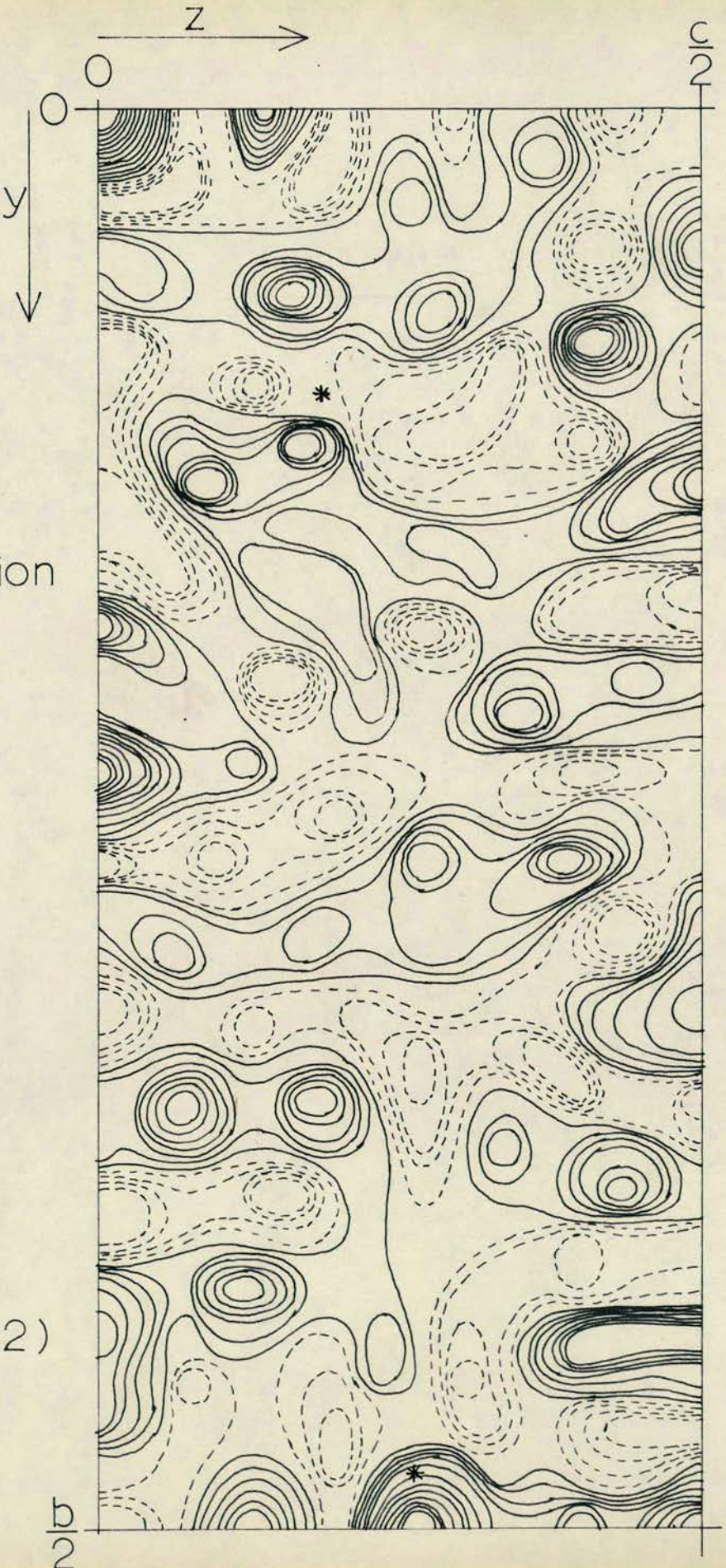


(fig 10)



(100)
Projection

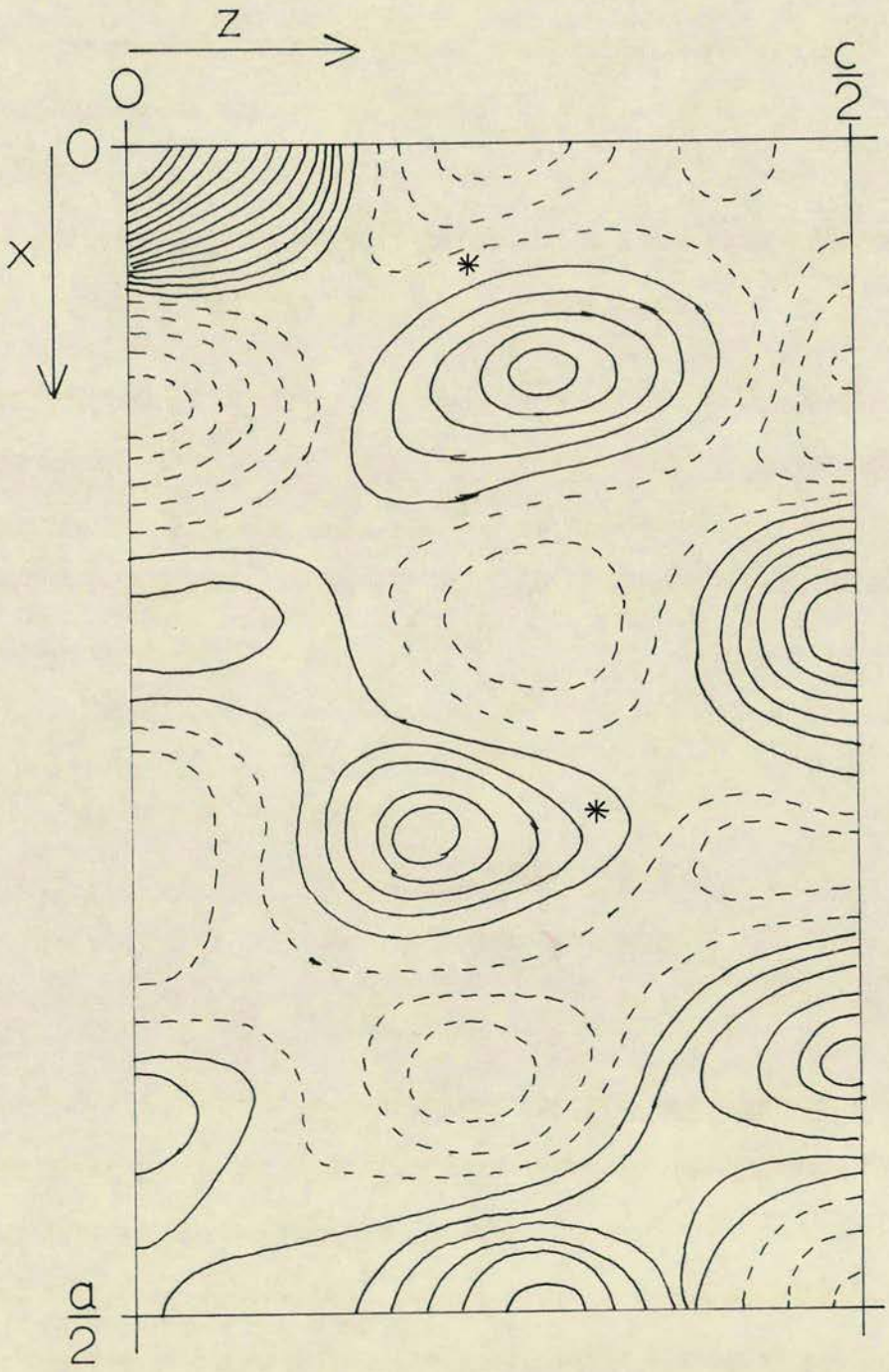
(fig 11)



(100)
Projection

(fig 12)

(010) Projection.



(fig 13)

The region of the three-dimensional Patterson map within 3 Å of the origin was now scrutinised. A model was made on a cork board, using wire spokes to support the pieces of plastic which represented the peaks found. All the symmetry-related peaks were included in the model. It was now compared to the projection Patterson maps, confirming that they were consistent with the three-dimensional synthesis. A search was now made for sets of six coplanar peaks centred on the origin, with 60° between adjacent peaks. For any set of 2.5 Å vectors there are two possible arrangements of the 1.5 Å vectors, so this ambiguity was resolved.

The orientation of one ring was readily determined. One of its 2.5 Å vectors lay parallel to a, so there was a mirror plane through the ring parallel to the (100) plane. Some peaks were therefore accidentally superimposed on each other. Omitting the centrosymmetrically related vectors, those obtained were:

	x	y	z
2.5 Å	24/120	0	0
	12/120	8/120	30/120
1.5 Å	0	5/120	18/120
	12/120	0	12/120

This accidental symmetry or near-symmetry had two consequences. Firstly, it made the orientation of this ring very obvious, since the peaks were weighted up even above the expected levels. Secondly, it made the determination of the exact orientation of the ring impossible, although it was suspected that the deviation from the symmetrical position was a small one since the peaks in the Patterson map were quite symmetrical. It could

be argued, however, that this roundness of the peaks was merely an artefact of the sharpening process, so little weight was given to this consideration.

It proved to be more difficult to establish the orientation of the second ring. It was clear, from packing considerations, that since the first ring lay roughly perpendicular to b, the longest axis of the unit cell, the second ring must be extended in this direction. An appropriate orientation was deduced, which was later found to be correct. The fit of the 2.5 Å vectors was less than convincing, so use was made of the 3 Å vectors which join opposite vertices of the ring in order to obtain more precise values. The vectors obtained were:

	x	y	z
2.5 Å	7/120	14/120	16/120
	16/120	9/120	18/120
	10/120	5/120	33/120
1.5 Å	5/120	9/120	0
	0	5/120	20/120
	12/120	0	14/120

A model of the molecule was now used to confirm that the two ring orientations were compatible. Several ways of joining rings in these orientations yield satisfactory geometry at the glucosidic linkage.

(c) The Harker Sections.

Although the correct structure was almost certain to fit the three Harker sections of the three-dimensional Patterson map very well, the

utilisation of the Harker sections in order to solve the structure presented a very difficult problem. This was because the image contained in each Harker section is on twice the scale of the unit cell, whereas the asymmetric unit of the Harker section covers one quarter of the unit cell, so that four images are superimposed on one another. There is also the problem of non-Harker peaks which accidentally appear in the section. The true Harker vectors are those between atoms related by the screw axes, which therefore appear in the sections $P(\frac{1}{2},y,z)$, $P(x,\frac{1}{2},z)$ and $P(x,y,\frac{1}{2})$ of the Patterson map.

An attempt was made to make better use of the Harker sections by the expedient of subtracting the values of, e.g. $P(29/60,y,z)$ from $P(\frac{1}{2},y,z)$. This procedure (T. R. R. McDonald, 1950) is based on the assumption that whereas a true Harker peak ought to have its maximum value at $x = \frac{1}{2}$, a peak which is accidentally close to the Harker section may have its maximum value at, say, $x = 29/60$. The difference map thus obtained should be rid of many of the background peaks, but some of the true Harker peaks may be removed by accident. In the event, attempts to locate rings in the known orientations failed to provide any useful information.

A much more powerful way of utilising the three Harker sections is to generate a symmetry minimum function (P. G. Simpson, R. D. Dobrott and W. N. Lipscomb, 1965). A three-dimensional map is produced by taking each point (x,y,z), comparing the projection of that point on to the three Harker sections and selecting the lowest value. Care must be exercised in displacing the origin of each of the three sections, since in space group $P2_12_12_1$ none of the screw axes passes through the origin, whereas for each Harker section the projection of the screw axis does. This map

was generated by hand, a simple but tedious process. The resultant map contained too many peaks to be interpretable. Overall, the Harker sections were of no use in solving the structure, although they did find use later, in order to check the plausibility of trial structures.

(d) The Projection Patterson Maps.

The Patterson summation in one, two or three dimensions may be expressed as:

$$\sum |F_{h_j}|^2 . \exp(-2\pi i \sum h_j u_j) \ ,$$

where h_j represents the Miller index or indices of a reflection and u_j a point in real space.

It was pointed out (A. L. Patterson, 1949) that there exists a related series:

$$\sum F_{h_j}{}^2 . \exp(-2\pi i \sum h_j u_j) \ .$$

This series measures the extent of symmetry about any point u_j. It can only be calculated when the h_j values used all belong to a centrosymmetric zone of reflections, in which case the two series are identical. The Patterson map may then be regarded as a map of the extent of centrosymmetry about each point in the unit cell. A peak at the point $2u_j$ in the Patterson map corresponds to a high measure of centrosymmetry about the point u_j in real space.

In space group $P2_12_12_1$ there are three centrosymmetric projections, i.e. the projections down the screw axes. If there is a group of atoms centrosymmetrically disposed about the point (x,y,z) in the unit cell, then a peak is expected in each of the Patterson projections, at the

following positions:

Projection	Co-ordinates		
(100)	-	$\frac{1}{2}$ - 2y	2z
(010)	2x	-	$\frac{1}{2}$ - 2z
(001)	$\frac{1}{2}$ - 2x	2y	-

The reason for the presence of such terms as ($\frac{1}{2}$ - 2x) is that if the conventional choice of origin is made for $P2_12_12_1$, then none of the screw axes passes through the origin. In the case of α-D-glucose (C. A. Beevers and T. R. R. McDonald, 1950 and T. R. R. McDonald, 1950) the identification of these vectors established the position of the ring in the unit cell, so this method is a powerful one.

The α,α-trehalose molecule was expected to consist of two chemically identical but crystallographically unrelated glucose rings. It can be seen (fig 1) that there are equatorial substituents on atoms C(2), C(3), C(4) and C(5) if the molecule is in the expected conformation. There are therefore eight atoms centrosymmetrically disposed about the centre of the ring. Similarly, about the centres of the C(2) - C(3), C(3) - C(4) and C(4) - C(5) bonds there are six atoms approximately related by a centre of symmetry. The corresponding numbers for the C(1) - C(2), C(5) - O(5) and C(1) - O(5) bonds are four, four and two respectively. These satellite peaks might be expected to assist in the identification of the peak corresponding to the centre of the ring. If the ring orientation is known, then the distribution of these satellite peaks about the central peak may be calculated.

The moderately sharpened projection maps (figs 9, 11 and 13) were not well resolved and the highly sharpened maps (figs 10 and 12) possibly contained spurious resolution, so pairs of maps were considered together. The (010) projection Patterson maps were very poorly resolved and so they were neglected except as a check on possible interpretations of the other maps.

From the (001) map the correct location of the first ring was readily obtained, i.e. the ring with a 2.5 Å vector parallel to a. All of the satellite peaks were found. An examination of the Harker section at $(x,y,\frac{1}{2})$ confirmed this result. Although packing considerations did dictate the position of the glucosidic linkage and the approximate position of the second ring, it was not possible to identify the centre-centre peak due to this ring. This was partly because this peak did not show up at all well and partly because the expected position of the peak was close to the intersection of two mirror planes in the (001) projection Patterson map. Thus if any peak were selected, then four possible positions of the centre of the ring in real space had to be considered.

Several possible locations of the ring were tried. For each of them there were four possible orientations of the ring, some more likely than others. There was also an ambiguity of labelling the atoms in the rings, for two ways were possible. Thus there were no fewer than thirty-two possible trial structures based on each assignation of the centre-centre vector! Structure factors were calculated for the more plausible trial structures and refinement by Fourier and difference Fourier syntheses was begun for the more promising ones. These attempts always failed, the refinement usually terminated with the conventional residual, R (defined

as $\sum F_{obs} - F_{calc} / \sum F_{calc}$) reduced to about 40 - 45%. The atoms of the second ring tended to have lower peak heights than those of the first ring in the electron density syntheses and to lie on negative ground in the difference Fourier maps. Calculating structure factors and a Fourier synthesis from only the atoms of the first ring indicated that the remaining atoms lay in the expected region, but the peaks obtained were very low and of poor resolution so that no further atoms were located. The failure to find the atoms of the second ring was the reason why a complete structure was not obtained by these methods.

The (100) projection Patterson map was now used to attempt to overcome this difficulty. This projection is down the 12.2 Å axis but is favoured by the accidental symmetry of the first ring. The 2.5 Å vector parallel to a causes four atoms to be projected almost on top of four others, as is shown in a drawing of the final structure (fig 18, following p.69). These four double atoms were expected to have a greater influence on the phases of the (0kl) reflections than eight single atoms would have had. A further advantage of working in this projection was that the four possible orientations of the unlocated second ring were very similar when viewed down the x axis.

Locating the centre of the first ring in the (100) projection led to an error. The value of ($\frac{1}{2}$ - 2y) for the centre-centre peak was known so only the value of 2z had to be found. There was only one large peak lying on the appropriate line in the (100) projection Patterson map and this interpretation did not agree well with the Harker section. This peak was utilised, however, and a trial structure was obtained which was refined to a residual, R = 33%. It then became clear that this structure was

incorrect, for the atoms tended to refine towards positions which did not make chemical sense. As the low value of the residual suggests, this structure was closely related to the correct solution. The molecule was in the correct orientation but was displaced along the z axis from its true position.

It was apparent that the error lay in the value of z for the rings and that the first ring had not been positioned correctly in the (100) projection. The two projection maps (figs 11 and 12) and the $(\frac{1}{2},y,z)$ Harker section (fig 4) were now examined together to obtain a new position for the ring centre. There was considerable uncertainty about the precise value of z for the centre of the first ring. The agreement between the Harker section and the projection maps was poor. A compromise value was obtained, which was later shown to be correct, approximately. Trial and error methods were used in an effort to obtain a more exact value, but since the atoms concerned did not constitute a very large proportion of the scattering matter, they were unsuccessful.

The positions where the centre-centre vectors should give rise to large peaks are marked on the maps shown (figs 9 - 13). It appears that this two-dimensional approach to the solution of the structure of α,α-trehalose was almost doomed to failure from the outset, for the only really convincing centre-centre peak is that due to the first ring in the (001) projection. The three-dimensional Patterson map projected on to (001) also fails to show the position of the centre-centre peak for the second ring clearly, despite the fact that this map was based on all the intensity data. In the end, the very good results for the first ring in the (001) projection were more of a hindrance than a help, for they

encouraged the belief that the second ring could also be located easily by this method, which led to many fruitless efforts to obtain a suitable fit of the (001) projection Patterson maps.

(e) Image Seeking Functions.

The sum function was applied to this problem, but it failed to yield any useful information. This was probably because the Patterson map did include a very large number of peaks which caused the background of the sum function to swamp the genuine information which it doubtless contained. An accumulation of single weight vectors is not likely to give rise to a large clear peak for a moderately complex structure such as this. The minimum function, which was tried next, is superior to the sum function in this respect.

It has been recommended that unsharpened Patterson syntheses be used for the generation of minimum function maps, by one authority (M. J. Buerger, 1959). For cellobiose, the only sugar structure to be solved by this method (R. A. Jacobson, J. A. Wunderlich and W. N. Lipscomb, 1961), sharpening was found to be essential. The usual exponential sharpening process failed to produce adequate resolution and so the gradient sharpening function was used instead, with success. It was in view of these conflicting opinions that it was decided to compute the second, less sharp, three-dimensional Patterson summation which was mentioned above (p.27). This new map, which was written on to magnetic tape by the KDF9 computer, was used for most of the minimum function calculations described, though some of the work was duplicated using the earlier, sharper, map.

TABLE 3

The Input Positions for the Minimum Function.

Set	x	y	z
A	-12/120	-4/120	-10/120
B	0	-2/120	-20/120
A	12/120	-4/120	-10/120
A	12/120	4/120	10/120
B	0	2/120	20/120
A	-12/120	4/120	10/120

****

The minimum function was first employed to try to discover the exact orientation of the rings. The relative positions of the six atoms of the first ring (Table 3) were now used as input positions in an attempt to discover the orientation of the whole molecule. Since a graphical superposition based on six atoms would have been very time-consuming, a numerical minimisation was undertaken instead. There was a mirror plane, perpendicular to a, and a centre of symmetry in both the Patterson map and the set of input positions. Consequently, the output map contained four related images superimposed on one another and the input atoms could be divided into two sets, A and B, of equivalent atoms. It was expected that a peak corresponding to an equatorial substituent atom would appear for both sets of input atoms, but that an axial substituent would appear for only one set. This was because the only axial substituent to the ring is atom O(1), bonded to C(1). Unfortunately, both axial and equatorial substituents appeared on both sets of atoms.

In an attempt to overcome this difficulty, it was argued that the axial substituent could be assigned to either an A or a B type atom. This defined the position of atom C(1) in the ring, and opposite to it was C(4), bonded to C(3) and C(5). The latter three atoms all bear equatorial substituents, so that ten atoms could be located. There were now two possible arrangements to consider. It was anticipated that one of them would give a markedly better fit with the three-dimensional Patterson map than the other. The two alternatives, however, gave equally good fits, although in both cases some slight rotation of the ring from its symmetrical position improved the peak heights at the atomic positions.

Lastly, an attempt was made to locate the ring in the unit cell. A computer program written by Dr. Candlin for the KDF9 computer was used to carry out a minimisation based on twelve atoms which constituted one ring and another related to it by the screw symmetry parallel to c. This approach also failed, probably due to three factors: firstly, the input positions were somewhat inaccurate; secondly, elsewhere in the unit cell there were other, smaller, groups of atoms in approximately the same orientation as those of the starting set; thirdly, the background of the Patterson map was too high. Thus the only achievements of the work done with the minimum function were to confirm the known ring orientations and to suggest that the glucose residues were in the expected conformation.

4. DIRECT METHODS OF PHASE DETERMINATION

(a) The Centrosymmetric Projections.

A new and different approach to the problem had much to reccommend it, so the triple product sign relationship (D. M. Sayre, 1952) was applied to the three centrosymmetric zones of reflections. Following roughly the terminology used by Professor Woolfson (in H. Lipson and W. Cochran, 1966) the relationship states that for three reflections of Miller indices h, k and h-k, with unitary structure factors U(h), U(k) and U(h-k) and signs S(h), S(k) and S(h-k) respectively, then:

$$S(h).S(k).S(h-k) \approx +1$$

where $\approx$ signifies "is probably equal to".

The probability, P, that a particular relation is correct has been shown (W. Cochran and M. M. Woolfson, 1955) to be given by:

$$P = \tfrac{1}{2} + \tfrac{1}{2}.\tanh\left\{\frac{W}{M^{3/2}}.\left|U(h).U(k).U(h-k)\right|\right\}$$

$$\text{where } W = \sum_{j=1}^{N} n_j^{\,3} \qquad M = \sum_{j=1}^{N} n_j^{\,2} \qquad n_j = f_j \Big/ \sum_{j=1}^{N} f_j$$

(n_j is the unitary scattering factor)

The structures of α-D-glucose monohydrate, which crystallises in space group $P2_1$ (R. C. G. Killean, W. G. Ferrier and D. W. Young, 1962) and β-D-glucose, which crystallises in space group $P2_12_12_1$ (W. G. Ferrier, 1963) have been solved by the use of sign relationships, utilising the method of coincidences (D. F. Grant, R. G. Howells and D. Rogers, 1957).

The average temperature factor and the scale factor obtained from the Wilson plot were now used to calculate unitary structure factors. The values for the (h00), (0k0) and (00ℓ) reflections were then divided by $\sqrt{2}$ in order to take account of the systematic absences which occur in these groups of reflections. For one projection at a time, the U(h) greater than 0.1 were marked out on a grid. By graphical superposition all the sets of reflections h, k and h-k were obtained. The cut-off value was chosen arbitrarily in order to restrict the list of relations to the more reliable ones.

One sign was now set arbitrarily for the largest U(h) in two of the three parity sub-groups (even,odd), (odd,even) and (odd,odd). In plane group pgg there are four possible choices of origin so this fixing of signs determined the choice of origin. Two or three other reflections were assigned symbols to represent unknown signs, following the "symbolic addition" procedure (I. L. Karle and J. Karle, 1963 inter alia). From these starting signs further signs were deduced using the triple product sign relationship. Since there were more relations than U(h) values, some confirmation of the correctness of the process was obtained and some of the unknown symbols were determined. A Fourier map was then calculated using the U(h) values as coefficients and the signs evaluated. It appeared that the amount of reflection data available was inadequate for a structure of this complexity, for none of the maps obtained was capable of interpretation.

(b) Phase Relationships for Non-centrosymmetric Reflections.

The first structure to be solved using phase relationships between non-centrosymmetric reflections (I. L. Karle and J. Karle, 1964) belonged to space group $P2_12_12_1$. This work demonstrated the viability of the methods which were subsequently described in more detail (J. Karle and I. L. Karle, 1966). These depended mainly on the use of two particular relationships, the so-called $\sum_2$ relationship and the tangent formula. The derivation of these, and other, relationships is based on the assumption that the electron density distribution is a non-negative function. Two further assumptions are made in order to simplify the mathematical calculations, firstly that the atoms, or more strictly squared atoms, are spherically symmetrical and consequently distinct, and secondly that all the atoms in the unit cell are of equal magnitude. The relaxation of these two conditions would not be expected to affect the validity of the relationships deduced, although it would alter the error, usually expressed as a variance, with which a phase would be deduced.

It has been shown (W. Cochran, 1955) that for three structure factors of Miller indices h, k and h-k the expected value of the phase φ_h is:

$$\langle \varphi_h \rangle \approx \varphi_k + \varphi_{h-k}$$

A simple form of the $\sum_2$ relationship averages all the pairs of large normalised structure factors, $|E|$, which contribute to the right hand side of the above expression. The average is to be understood as the value which gives maximum clustering of the contributions of individual pairs, i.e. there should be the minimum possible deviations of these contributors from the average value. A more sophisticated variant includes a weighting

term to allow for the fact that the larger the normalised structure factors $|E_k|$ and $|E_{h-k}|$ are, the smaller is the probable error in φ_h:

$$\varphi_h \approx \frac{\sum_{k_r} |E_k . E_{h-k}| . (\varphi_k + \varphi_{h-k})}{\sum_{k_r} |E_k . E_{h-k}|}$$

where k_r implies that k ranges only over those vectors associated with large $|E|$ values.

The normalised structure factors are not restricted to one octant of reciprocal space, but as they change octants their phases change. If the Miller indices of a reflection are $(h_1 h_2 h_3)$ then, using the conventional definition of the axes in space group $P2_12_12_1$, the following changes occur:

(h_1+h_2)	(h_2+h_3)	$(h_1 h_2 h_3)$	$(\bar{h}_1 h_2 h_3)$	$(h_1 \bar{h}_2 h_3)$	$(h_1 h_2 \bar{h}_3)$
even	even	α	$-\alpha$	$-\alpha$	$-\alpha$
even	odd	α	$-\alpha$	$\pi-\alpha$	$\pi-\alpha$
odd	even	α	$\pi-\alpha$	$-\alpha$	$\pi-\alpha$
odd	odd	α	$\pi-\alpha$	$\pi-\alpha$	$-\alpha$

If the signs of all three indices change, then α changes to $-\alpha$.

The tangent formula (J. Karle and H. Hauptman, 1956 and 1958) may be expressed:

$$\tan \varphi_h = \frac{\sum_{k_r} |E_k . E_{h-k}| . \sin(\varphi_k + \varphi_{h-k})}{\sum_{k_r} |E_k . E_{h-k}| . \cos(\varphi_k + \varphi_{h-k})}$$

The numerator and denominator of the right hand side of this expression are proportional to the probable values of $|E_h| . \sin \varphi_h$ and $|E_h| . \cos \varphi_h$ respectively. It was pointed out that it is thus possible to obtain an

unscaled value of $|E_h|^2$. When a set of phases has been calculated by means of the tangent formula, these $|E_h|_{calc}$ values may be summed and rescaled to $\Sigma|E_h|_{obs}$. A residual may be calculated in the usual way, as a measure of the self-consistency of the set of phases obtained (J. Karle and I. L. Karle, 1966). There is a close similarity between the tangent formula and the Σ_2 relationship, for they both make use of the same pairs of k and h-k reflections. The convenience of the tangent formula is that it can readily be calculated by computer, whereas the averaging or clustering process is more suited to hand calculation.

(c) Partial Solution of the Structure by Phase Relationships.

The first necessary step was to convert the list of observed intensities into normalised structure factor magnitudes, $|E_h|$. Squared structure factor magnitudes, $|F_h|^2$, were readily obtained using the scale factor and average temperature factor which had been deduced from the Wilson plot. These were then converted into normalised structure factor magnitudes by means of the equation:

$$|E_h|^2 = \frac{|F_h|^2}{\epsilon . \sum_{j=1}^{N} f_j^2(h)}$$

where ϵ is a factor to correct for space group extinctions, which was discussed above (p.41).

A program to carry out this calculation was written in Atlas Autocode for the KDF9 computer. There were found to be 238 $|E_h| \geq 1.50$ of which 65 were greater than 2.00. A list of the largest $|E_h|$ values is presented later in this thesis (Appendix I).

Two further programs were written in Atlas Autocode for the KDF9 computer. The first produced a $\sum_2$ listing. For each h all the contributing pairs k, h-k were listed with the value of $|E_h.E_k.E_{h-k}|$ on which the accuracy of the calculated phase angle depends. The listing was restricted to values of $|E_h| \geq 1.50$, for the computer time required by the listing increased with the cube of the number of $|E_h|$ values used. The second program could extend or refine a set of phases by means of the tangent formula. The program printed out the number of contributing pairs for each φ_h as well as the value. $|E_h|_{calc}$ values were also printed out, with the residual mentioned above (p.44) and the scale factor used. Although one of the advantages of the tangent formula is that it allows several iterations to be performed during one entry to the computer, this could not be arranged due to the limited size of the store of the computer.

The phase determining procedure was based closely on that derived by the Karles (J. Karle and I. L. Karle,1966). The $\sum_1$ relationship was used first in order to determine, if possible, the signs of those structure factors in the centrosymmetric zones whose Miller indices were all even. This formula may be expressed:

$$S(0,2k,2l) \approx \sum_{h_j} (-1)^{h_j+k}.(|E_{h_j k l}|^2 - 1)$$

The magnitude of the sum gives an indication of the accuracy of the sign determined. The results of the application of this relationship are shown (Table 4); the phases determined did not enter into many $\sum_2$ relations, and so they were not used except as confirmations of correctness later.

TABLE 4

The Results of the Application of the Σ_1 Relationship.

h	k	l	|E|	NC	Σ	IS	CS
10	0	0	2.12	21 9	-6.5 -16.2	-	-
0	18	6	1.64	14	11.7	+	+
0	14	0	2.18	15 9	5.2 3.3	+	+
10	8	0	1.50	10	7.3	+	+
4	6	0	2.28	10	-7.1	-	-
10	16	0	1.55	9	6.5	+	+
0	4	8	2.35	15	5.9	+	+
0	16	2	1.86	15	-5.8	-	-
10	14	0	1.77	9	-4.7	-	-
10	2	0	2.61	10	2.9	+	+
0	4	4	1.70	16	-2.7	-	+
0	2	8	1.94	15	-2.0	-	+
6	4	0	1.52	10	-1.8	-	+
6	18	0	1.55	9	1.8	+	+
2	0	8	1.93	22	-1.1	-	+
4	20	0	1.96	9	0.6	+	-

NC represents the number of terms contributing,

and IS and CS the indicated and correct signs.

It has been noted (e.g. G. Germain, P. Main and M. M. Woolfson, 1970) that it is very important that a phase determination should get off to a good start. There were no clear guides as to how this might be achieved, so some empirical rules were established to govern the choice of the starting set of phases. It was clear that four centrosymmetric reflections could be used to fix the origin and specify the enantiomorph. Reflections were chosen from the appropriate parity sub-groups which had high $|E_h|$ values and took part in as many relations as possible. The choice of further reflections to be assigned unknown symbols to represent their phases was a very open one. Three main conditions were considered:

(i) all possible values of each of the Miller indices must be reached quickly;

(ii) new phases must be generated by relations with the highest possible values of the product $|E_h.E_k.E_{h-k}|$;

(iii) as many phases as possible must be generated in the least possible number of iterations.

It was therefore necessary to consider a number of possible additions to the starting set in turn, to discover which would best satisfy these conditions. Eventually two non-centrosymmetric reflections were added to the set (see Table 5, p.48).

For the first application of the Σ_2 relationship only the 65 $|E_h|$ values ≥ 2.00 were considered. Of these, three were not involved in any relations, so 96 relations involving 62 $|E_h|$ were used. From the set of six phases 23 new phases were rapidly deduced. The approximate value of the unknown symbol a was found to be 0. The use of the Σ_2 relationship was now extended, for one iteration only, to the $|E_h|$ values down to 1.50.

TABLE 5

The Starting Set of Phases for Symbolic Addition.

h	k	ℓ	φ_h	E_h	Nr
0	4	3	0	2.58	9
0	9	2	$\frac{\pi}{2}$	2.45	6
5	0	2	0	3.44	9
9	5	0	$\frac{\pi}{2}$	3.25	10
6	8	3	a	2.86	15
4	13	4	b	2.53	8

Nr represents the number of relations in which h appeared.

****

In this calculation phases were only accepted as correct when there were two or more consistent indications. The aim of this extension of the use of the Σ_2 relationship was to evaluate the unknown symbol, b, which was found to be $\frac{3\pi}{2}$. There was now only one set of phases to be fed into the tangent formula program, rather than several sets.

When the tangent formula was applied to the 93 φ_h values established so far, no refinement took place. The value of b was now changed by $\frac{\pi}{6}$ radians, so that two new slightly different sets of phases were obtained. These two sets were equally self-consistent, so one of them was chosen arbitrarily for further work. If it had proved necessary then the other set would also have been used. Altogether seven cycles of tangent formula calculations were carried out, as described below. The criteria for rejecting a calculated phase were either that the value obtained varied

greatly from one cycle to the next or that $|E|_{calc} < \frac{1}{3}|E|_{obs}$ or, in the case of a new phase, that there were less than three or four contributing k, h-k pairs.

Cycle 1: The set of 93 phases was refined. The mean shift in the 73 non-centrosymmetric phases, MS(73) = 0.059 radian.

Cycle 2: The 93 phases were again refined, MS(73) = 0.039 radian. Phases were calculated for 73 new reflections for which $|E_h| \geqslant 1.80$, of which 36 were accepted.

Cycle 3: 129 phases were refined, of which 4 were rejected. For the others MS(101) = 0.128 radian.

Cycle 4: 125 phases were refined, MS(101) = 0.069 radian.

Cycle 5: 125 phases were used but not refined. The phases of the other 113 reflections for which $|E_h| \geqslant 1.50$ were calculated, of which 52 were accepted.

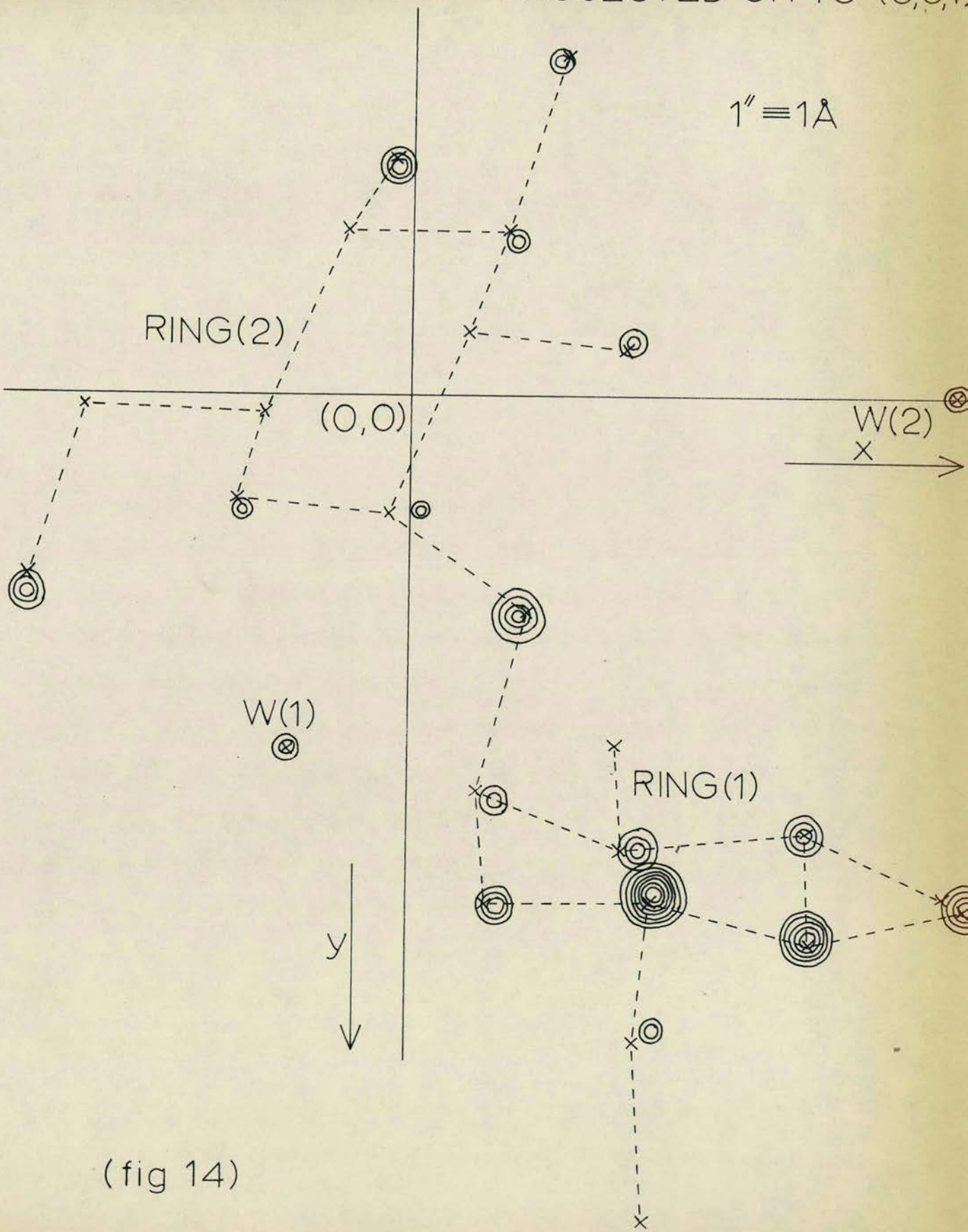
Cycle 6: 177 phases were refined, MS(137) = 0.098 radian.

Cycle 7: The phases of the remaining 61 reflections for which $|E_h| \geqslant 1.50$ and the 82 reflections for which $1.50 > |E_h| \geqslant 1.38$ were calculated. Of these, 114 phases were accepted, making a total of 291 phases determined.

It would have been preferable to have continued the refinement but the computing time required was now estimated to be very large, so instead the phases were used, with the $|E_h|$ values as coefficients, to compute an E-map (I. L. Karle, H. Hauptman, J. Karle and A. B. Wing, 1958). The use of normalised structure factors in place of the square roots of the observed intensities as Fourier coefficients is analogous to the "point atom at rest" sharpening of a Patterson summation. It has the same

effect of increasing the apparent resolution of the map. The eighteen largest peaks in this map are shown (fig 14). There are very many smaller peaks in the map, for the cut-off level is just above the height of the background. The most striking feature of this map is readily identified as the glucose ring which had already been located by Patterson methods. All the carbon atoms were shown, but O(2), O(3) and O(6) were missing. Peaks only slightly below the cut-off level were found at the expected positions of O(2) and O(3) but the position of O(6) could not be established unequivocably. Its tentatively chosen position was later found to be correct.

If more confidence had been placed in this E-map then it would have been adequate to solve the structure completely. Instead, a wrong line of attack was followed. The main reason for distrusting the E-map was the wide variation in the peak heights of the correctly located atoms. Other such maps in the literature generally showed closely uniform peak heights. The second reason for failing to make full use of the map was that it proved conclusively that the earlier Patterson approach had led to correct conclusions. It thus seemed very unlikely that the second ring, which did not show up at all well in the E-map, would not give rise to a good centre-centre peak in the (001) projection Patterson map. In addition the E-map had now removed many of the uncertainties which had beset the earlier Patterson work, for the geometry of the first ring was now clearly established. Attempts to interpret the remaining peaks in the E-map using ring centre positions erroneously deduced from the (001) projection Patterson map failed. A Fourier synthesis using phases from the atoms of the first ring only was computed. This showed diffuse peaks



(fig 14)

in approximately the correct positions, but the resolution was too poor to allow the correct solution to be obtained.

An analysis of the accuracy of the phases determined in this way appears later (Table 8, p.57) and a full list of all the phases is given (Appendix I). Summarising the results, of the sixty phases of centrosymmetric reflections determined only three were wrong. For the non-centrosymmetric reflections the average error was 0.62 radian, i.e. 35.6°. The most disturbing feature of this analysis is that the errors are no smaller than average for the largest $|E_h|$. A graph of the distribution of errors for the non-centrosymmetric reflections is shown (fig 15).

(d) The Multan System.

This system of three programs, written in Fortran IV, was developed by G. Germain, P. Main and M. M. Woolfson to carry out automatic phase determinations for non-centrosymmetric crystal structures. The first of the programs, designated SIGMA2, reads in $|E_h|$ values and space group information. It produces a list, which is stored in the computer, of all possible Σ_2 phase relations. Since this list may be very long, it is possible to restrict it. One limitation is that the user may specify that the value of the product $|E_h.E_k.E_{h-k}|$ must be greater than a given figure, and another that only a specified number of relations, starting with the most reliable and working downwards, be kept. These restrictions may be used to eliminate many of the less reliable relations, which are unimportant, with a consequent saving of computing time and store space.

The second program, CONVERGE, makes use of the output from the first and determines the types of reflection necessary to specify the origin.

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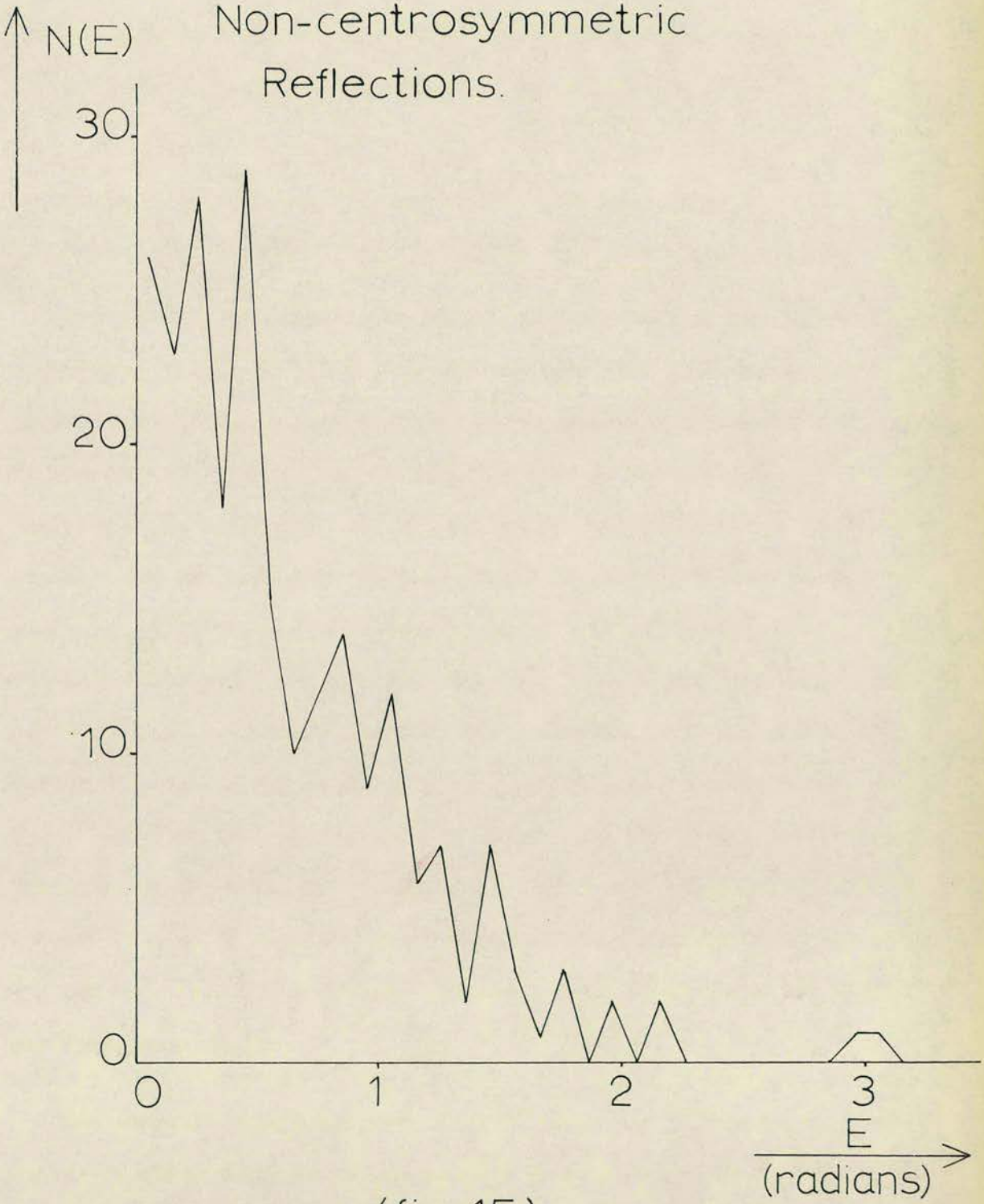
Graph of Distribution of Errors in Calculated Phases of Non-centrosymmetric Reflections.



(fig 15)

It works out any restrictions on phase values due to space group symmetry and selects the appropriate Σ_1 formula. It applies the Σ_1 formula and works out the probability that each phase calculated thus is correct. The Σ_1 formula for space group $P2_12_12_1$ has been given above (p.45) and the probability of a sign so evaluated being positive is given by:

$$P_+(0,2k,2\ell) = \tfrac{1}{2} + \tfrac{1}{2}.\tanh\left\{\frac{W}{2M^{\frac{1}{2}}}\cdot|E_{0,2k,2\ell}|\cdot\sum_{h_j}(-1)^{h_j+k}.(|E_{h_jk\ell}|^2 - 1)\right\}$$

where W and M are as above (p.40).

The program now proceeds to find a good set of starting phases. The quantity α_h, which is related to the variance of φ_h (J. Karle and I. L. Karle, 1966) is estimated for each reflection in the list (G. Germain, P. Main and M. M. Woolfson, 1970). The reflection with the smallest α_h is eliminated and the values for the remaining reflections are adjusted if necessary. This procedure is re-iterated until only the starting phases are left. As each reflection is eliminated, those which remain a e checked to ensure that they contain all the reflections necessary for origin definition. If not, the reflection just eliminated is restored as one of the origin-defining reflections. Other reflections may be added to the starting set if their value of α_h when they are eliminated exceeds a specified limit. These additional reflections have unknown phases, so they are given all possible combinations of the values $\pm\frac{\pi}{4}$ and $\pm\frac{3\pi}{4}$, except for centric reflections for which there are only two possible phase angles.

The tangent formula program, FASTAN, makes use of the output from the two earlier programs and by several successive cycles of refinement

and extension developes each set of starting phases into a set of phases for all the reflections. Each phase is given a weight. The starting set are given weights of unity, phases from the Σ_1 calculation are given the weight of $2.|P - \frac{1}{2}|$, and undetermined phases have zero weight. The phases in the starting set are kept constant until the last two cycles of the refinement but the others derive their values and weights from the weighted tangent formula:

$$\tan\varphi_h = \frac{\sum_{k_r} w_k . w_{h-k} . |E_k . E_{h-k}| . \sin(\varphi_k + \varphi_{h-k})}{\sum_{k_r} w_k . w_{h-k} . |E_k . E_{h-k}| . \cos(\varphi_k + \varphi_{h-k})} = \frac{T_h}{B_h}$$

$$w_h = \tanh(\tfrac{\alpha_h}{2}) \qquad \alpha_h = |E_h| . (T_h^2 + B_h^2)^{\frac{1}{2}}$$

The effect of weighting the tangent formula is to lead to a much faster convergence on the final result than with an unweighted calculation.

As a measure of the internal consistency of the set of phases a "figure of merit" is calculated as:

$$F_{abs} = \frac{\sum_h \alpha_h - \sum \alpha_r}{\sum_h \alpha_e - \sum \alpha_r}$$

where $\sum \alpha_e$ is the sum of the α_h values used in CONVERGE
and $\sum \alpha_r$ is the value of $\sum_h \alpha_h$ assuming random phases.

F_{abs} should have the value zero for a purely random set of phases and unity if $\sum_h \alpha_h$ is equal to its expectation value. The tangent formula, however, tends to maximise the internal agreement, so that although it is to be expected that the correct set of phases will have $F_{abs} = 1.1$

or 1.2, the converse does not hold. On the other hand, a set of phases with F_{abs} much less than unity is very unlikely to be correct, so the figure of merit does have some use.

(e) The Complete Solution of the Structure.

A program written by Dr. Scott converted the full set of intensity data into normalised structure factors. Rather than using a Wilson plot, the program utilised a K-curve, a method which is generally likely to lead to a superior phase determination (J. Karle, 1970). The $|E_h|$ values calculated in this way were only slightly altered from the earlier ones, and it is the later list which is recorded herein (Appendix I). The output from this program included an analysis of the distributions of the $|E_h|$ values, which is shown below (Table 6).

TABLE 6

Normalised Structure Factor Distributions.

	Theoretical		Observed
	Centric	Non-centric	
$\overline{E^2}$	1.000	1.000	0.993
$\overline{E^2-1}$	0.968	0.736	0.771
$\overline{\vert E \vert}$	0.798	0.886	0.868
$E > 1$	32.0%	36.8%	34.0%
$E > 2$	5.0%	1.8%	2.8%
$E > 3$	0.3%	0.01%	0.14%

The 282 $|E_h| > 1.40$ were fed into SIGMA2 and 2530 relations were found of which the 1500 with the largest $|E_h.E_k.E_{h-k}|$ were selected for the phase determination procedure in order to avoid overflowing the store of the computer. One reflection, (2,3,1), was involved in 111 relations, whereas at the other extreme (0,16,0) was involved in none; altogether 30 reflections were involved in less than four relations.

The CONVERGE program now found $\varphi_{(10,0,0)} = \pi$ with 98% probability and $\varphi_{(0,18,6)} = 0$ with 81% probability, using the Σ_1 relationship. The minimum level for acceptance of such phases had been set at 80% probability. The usefulness of the Σ_1 formula was very much restricted by limiting the data used to the $|E_h| > 1.40$; the earlier results (Table 4, p.46) were more encouraging than this.

The complete set of starting phases is shown below (Table 7). It includes the two signs determined by the Σ_1 relationship, four phases of centrosymmetric reflections which were used to fix the origin and specify the enantiomorph and two unknown phases of "good" starting reflections. There were thus eight sets of starting phases, which differed in the values assigned to the unknown phases. It might be noted that only three of the six reflections in the previous starting set (Table 5, p.48) were included in the new list, so that the two phase determinations were quite independent.

Phase determinations using the eight different starting sets were carried out simultaneously using FASTAN. Instead of eight different sets of phases, four pairs were obtained. This was because the two unknown phases, $\varphi_{(0,4,3)}$ and $\varphi_{(1,8,1)}$ were somehow related to each other.

TABLE 7

The Starting Set of Phases in the Multan Method.

h	k	ℓ	φ	Weight	
10	0	0	π	0.97	
0	18	6	0	0.61	
9	5	0	$\frac{\pi}{2}$	1	Used before
11	4	0	$\frac{\pi}{2}$	1	
0	17	1	$\frac{\pi}{2}$	1	
5	0	2	0	1	Used before
1	8	1	$\pm\frac{\pi}{4}, \pm\frac{3\pi}{4}$	1	
0	4	3	$0, \pi$	1	Used before

****

The four pairs of sets of refined phases yielded figures of merit of 0.8389, 0.8409, 0.8816 and 0.9750. The best value of the figure of merit was thus rather lower than was expected for a correct set of phases. An attempt could have been made to attain a higher figure of merit by selecting another reflection to replace, say, (1,8,1), or by using a larger number of unknown phases. Before this was tried, it was decided to compute an E-map using the best set of phases, i.e. that with figure of merit of 0.9750. The accuracy of the set of phases used was comparable to that of the phases deduced earlier. An analysis of both sets is shown (Table 8). The limits for the acceptance of a phase were less rigorous for the later set of phases, which is consequently at a slight disadvantage in the comparison.

TABLE 8

Analysis of the Accuracy of both Phase determinations.

A. Centrosymmetric:

First Set		Multan		ND Common	First NW	Multan NW
ND	NW	ND	NW			
60	3	65	11	50	3	6

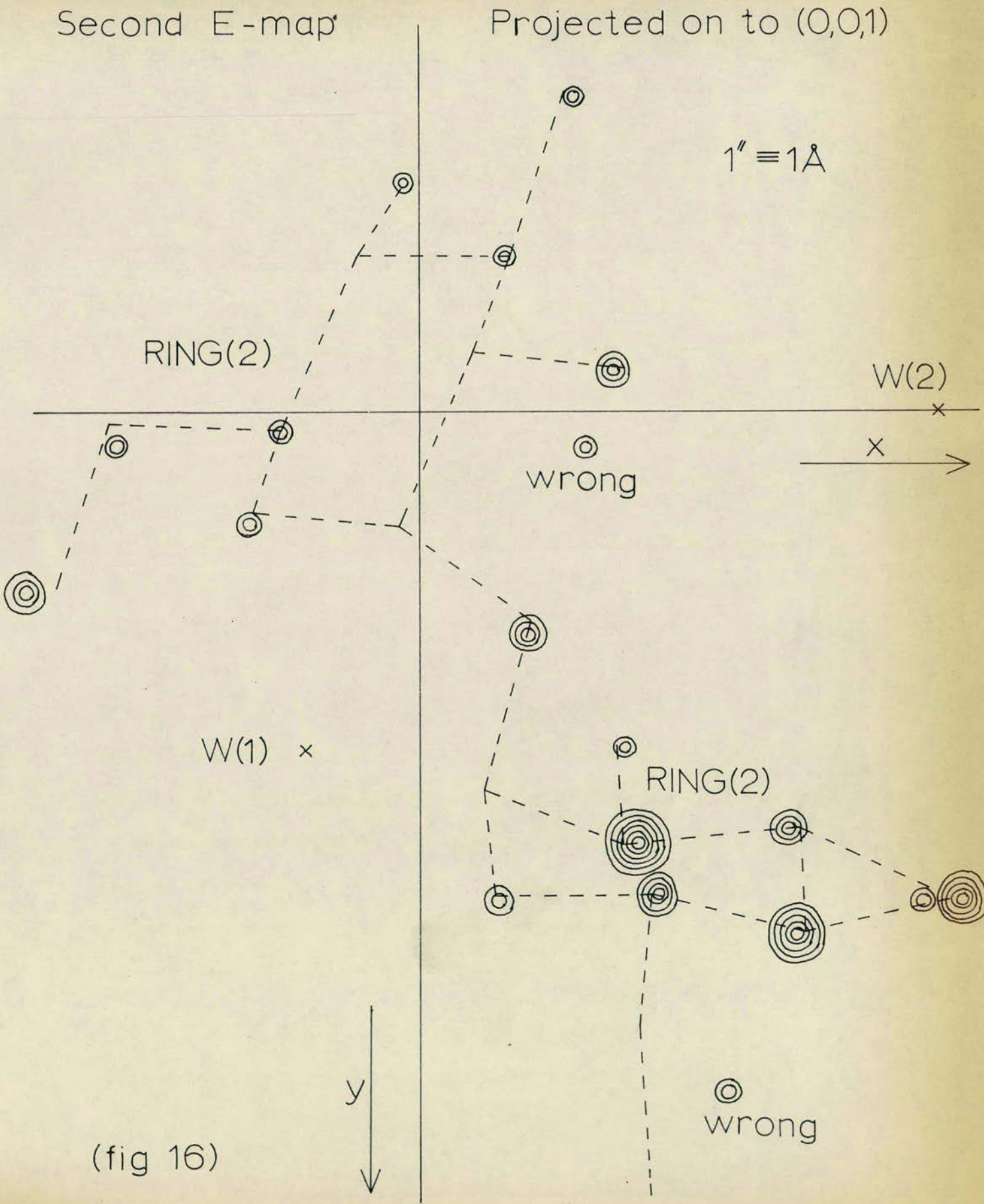
B. Non-centrosymmetric:

E	First Set		Multan		ND Common	First Error	Multan Error
	ND	Error	ND	Error			
≥2.5	6	42.5°	6	33.3°	6	42.5°	33.3°
2.2	15	31.5	17	37.8	15	31.5	35.9
2.0	16	36.9	16	36.2	16	36.9	36.2
1.9	7	52.4	7	55.4	7	52.4	55.4
1.8	20	27.6	21	40.4	20	27.6	40.6
1.7	32	32.4	34	45.7	32	32.4	47.1
1.6	21	31.7	24	34.2	21	31.7	33.7
1.5	40	30.3	38	44.6	37	27.6	45.2
1.4	44	38.0	37	38.7	34	36.1	37.4
1.3	30	46.7	-		-		
TOTAL:	231	35.6	200	40.8	188	32.9	40.8

ND = number of phases determined, of which NW are wrong.

The calculated phases were accepted for all but 17 of the 282 $|E_h|$, the exceptions being those phases with the largest estimated errors, i.e. the lowest α_h values. The E-map computed with these 265 normalised structure factors as coefficients contained peaks which were readily ascribed to the first ring of the α,α-trehalose molecule. The nineteen largest peaks in the E-map are shown in a diagram (fig 16). This information, in conjunction with a model of the molecule, was sufficient to locate the second glucose ring. Two of the weakest peaks in this map did not correspond to any atom in the correct structure. Further atoms were located by examining the map at expected atomic positions and finding lesser peaks there. Although O(6') had been tentatively identified, the peak corresponding to C(6') was absent, so both these atoms were omitted. Twenty atoms were located, the exceptions being O(6), C(6'), O(6'), O(W1) and O(W2).

Structure factor calculations for all the intensity data were based on these twenty atoms, all assigned thermal vibration parameters B = 2.3 $Å^2$. The residual was R = 42.7%. An electron density synthesis calculated from these structure factors contained five peaks in addition to the input information. These peaks were identified as the remaining five atoms of the asymmetric unit of the structure. The indicated shifts in the positional parameters of the other atoms generally led to closer agreement with the expected molecular geometry, with the solitary exception of O(1) and C(1). Thus the complete structure was elucidated.


Second E-map
Projected on to (0,0,1)
1″ ≡ 1Å
RING(2)
W(2)
x
wrong
W(1)
RING(2)
y
wrong

(fig 16)

5. THE REFINEMENT OF THE STRUCTURE

The atomic scattering factors which were used to calculate structure factors during the refinement were obtained from the literature (Oxygen: A. J. Freeman, 1959; Carbon: J. Berghuis et al., 1955; Hydrogen: R. McWeeny, 1951). In the collection of the data it was assumed that there would be no significant differences between the intensities of the Friedel pairs I_h and $I_{(-h)}$; this assumption was followed by the arbitrary specification of the enantiomorph in the phase determining process. It was found that the co-ordinates obtained described the "correct" enantiomorph. The structure deduced by the Multan method was modified so that the new origin was that used in the earlier work.

The twenty-five carbon and oxygen atoms in the asymmetric unit were now used to calculate structure factors and hence a three dimensional electron density synthesis. All the atoms were assigned the isotropic temperature factor B = 2.3 Å^2. The residual fell to R = 25.6%, clearly indicating the correctness of the structure. There were many indications of shifts in the fractional co-ordinates of the atoms, especially for C(1) and O(1) which required quite substantial shifts. A further round of structure factor and Fourier computation was now effected, which reduced the residual to R = 20.4%. It was thought that the positional parameters were sufficiently close to their correct values for refinement by the method of least squares (E. W. Hughes, 1941) to be successful.

Various weighting schemes for the refinement of structure factors by the method of least squares have been suggested (e.g. D. W. J.

Cruickshank et al., 1961). In the present case the method followed was very simple. The standard deviations of different ranges of structure factor magnitudes had already been estimated (Table 1, p.22). It is appropriate to weight each $|F_h|$ according to the square of the reciprocal of its estimated standard deviation. The weight for each $|F_h|$ was calculated and stored in the computer. The effect of this scheme was to reduce the weights of the very weak and very strong reflections. It failed to take into account any variation of the accuracy of the intensities with θ.

Three cycles of refinement using a full matrix least squares calculation were carried out, which may be summarised:

Cycle	Input R	Output R	$\sum w\Delta^2$	NP
1	20.4%	13.1%	20180	77
2	13.1%	10.0%	9053	101
3	10.0%	9.7%	7638	101

where NP = the number of parameters varied.

In the first cycle only the positional parameters, the overall isotropic temperature factor and the scale factor were allowed to vary. No damping factor was applied to the calculated shifts. Some large positional shifts were made, the largest being one of fourteen times the estimated standard deviation for the fractional co-ordinate, z, of C(1) up the short axis. This shift moved C(1) towards its expected position.

In the second cycle the isotropic temperature factors of individual atoms were allowed to vary. The position of C(1) again altered more than

that of any other atom, moving it close to its final position. This was reflected in its temperature factor, which was significantly larger than those of the other ring atoms. The two water molecules appeared to be vibrating most vigorously of all the atoms.

In the third cycle the indicated shift in z for C(1) was three estimated standard deviations. The latter quantity had, as is usual, decreased considerably during the refinement. None of the other shifts in positional parameters was much greater than one standard deviation. The thermal vibration parameter for C(1) fell by five estimated standard deviations to attain a value comparable to those for similar atoms. It appeared that this stage of the refinement had almost converged.

A three dimensional difference Fourier synthesis was now computed in order to locate the hydrogen atoms before extending the refinement of the other atoms to anisotropic thermal parameters. In fact two such syntheses were needed to locate all 26 hydrogen atoms in the asymmetric unit of the structure. In the first map, the biggest peaks were rather diffuse with heights of about 0.6 to 0.7 electrons Å^{-3}. These occurred in the positions where hydrogen atoms were expected. The fourteen hydrogen atoms bonded to carbon atoms all showed up clearly. Thirteen of these had C - H bond lengths in the range 0.89 to 1.08 Å and the exception was 1.31 Å long. This was clearly too long, so the bond length was reduced to 1.1 Å without changing the bond direction by shifting the hydrogen atom. This new position still fitted the Fourier map well. Ten of the hydrogen atoms bonded to oxygen atoms were located in hydrogen bonds, at a mean O - H bond length of 0.98 Å. As some of these atomic

positions were rather uncertain, probably due to the effect of the thermal vibrations of the oxygen atoms, all these hydrogen atoms were located on the line between the two oxygen atoms of the hydrogen bond, with a bond length of 0.98 Å to the nearer oxygen atom.

It was necessary to compute a second round of structure factor calculation and difference Fourier synthesis in order to locate the other two hydrogen atoms. Their positions were dictated by the hydrogen bond pattern but it was thought that it would be more satisfactory to obtain experimental confirmation of their correctness. The twenty-four hydrogen atoms located so far were included in the calculations with isotropic temperature factors of 2.5 $Å^2$. The residual fell to 8.4% for all the reflections and to 9%, 9% and 10% for the (hk0), (h0ℓ) and (0kℓ) reflections respectively. The analysis of agreement showed that the residual ranged from about 6% for the low angle reflections to 13% at the highest angles. The major systematic error remaining in the data was the lack of any allowance for anisotropic thermal vibration by the atoms, which would have most effect on the higher angle reflections. The largest peaks in the second difference Fourier map had heights of the same magnitude as those attributed to hydrogen atoms in the first map. They were, however, identified as the consequence of anisotropic thermal vibration of the atoms O(3), O(4), O(2'), O(3') and O(4'). The remaining hydrogen atoms were both located with peak heights of 0.4 to 0.5 electrons $Å^{-3}$.

In introducing anisotropic thermal vibration, the number of parameters used to describe each atom is increased from four to nine, if the atomic number is regarded as fixed. It was not possible to use the full matrix least squares calculation with the large number of parameters which it

was now desired to vary. A program which utilised the block diagonal approximation was employed instead. It was clear that the refinement was sufficiently advanced for the contributions of off-diagonal terms to be very small. Four cycles of refinement were performed, which may be summarised as follows:

Cycle	R_{input}	$\sum w\Delta^2$
1	8.38%	6999
2	5.99	3428
3	5.71	3026
4	5.69	3024

Three positional parameters and six thermal parameters were refined for each of the carbon and oxygen atoms during the first three cycles. The overall scale factor was also varied. In the third cycle the largest shift in a positional parameter was about three-quarters of an estimated standard deviation and that in a thermal parameter was about one estimated standard deviation.

In the final cycle the positional and isotropic thermal parameters of the hydrogen atoms were also refined. The largest positional change was about 0.25 Å which indicated that the hydrogen atoms were roughly correctly placed. Several of the thermal parameters of the hydrogen atoms became negative but these had only been included in the refinement since in order to omit them it would have been necessary to alter the program. For the carbon and oxygen atoms the largest shifts in both the thermal and positional parameters were now about half an estimated standard deviation so that the refinement was now effectively terminated.

These final parameters, with the exception of the thermal parameters of the hydrogen atoms which were all reset to 2.5 $\mathring{A}^2$, were used to calculate a final set of structure factors and hence final electron density and difference syntheses. The structure factors are shown later in this thesis (Appendix IV). The analysis of agreement for them is shown (Table 9) and the final atomic parameters are listed (Tables 10, 11 and 12). The final value of the residual was R = 5.5%.

Soon after this work was completed, two separate groups of crystallographers in the United States solved the structure independently, also by direct methods. Dr. D. C. Rohrer, in Pittsburg, collected data using a diffractometer with Cu K_α radiation to $2\theta = 130^\circ$. Dr. G. M. Brown, in Oak Ridge, also employed a diffractometer but used a Mo target. He thus collected well over 3,000 independent reflections. Both obtained final residuals rather better than the present figure (D. C. Rohrer, 1970; G. M. Brown, 1971). There is very good agreement between the three sets of parameters, which is indicated later (Appendices II and III). The discussion of the structure which follows was written before these other sets of parameters became available, but the later results did not affect the conclusions reached.

The form of the anisotropic thermal parameters was:

$$\exp(-B_{11}.h^2 - B_{22}.k^2 - B_{33}.l^2 - B_{23}.k.l - B_{31}.l.h - B_{12}.h.k)$$

where $B_{11} = 2.\pi^2.a^{*2}.U_{11}$

$$B_{23} = 4.\pi^2.b^*.c^*.U_{23}$$

$$a^* = \frac{1}{a}$$

TABLE 9

Analysis of Agreement for the Final Structure Factors.

(i) Against $\sin^2\theta$:

$\sin^2\theta$	$\Sigma\|F_{obs}\|$	$\Sigma\|F_{calc}\|$	$\Sigma\|F_o-F_c\|$	R
0.0 - 0.1	35621	36850	1745	0.05
0.1 - 0.2	44371	44022	1900	0.04
0.2 - 0.3	29594	29048	1407	0.05
0.3 - 0.4	33282	33654	1672	0.05
0.4 - 0.5	34434	35273	1757	0.05
0.5 - 0.6	28926	29209	1612	0.06
0.6 - 0.7	23287	22996	1401	0.06
0.7 - 0.8	21617	21045	1457	0.07
0.8 - 0.9	20476	19637	1477	0.07
0.9 - 1.0	16987	16897	1362	0.08

(ii) Against $|F|$:

Fraction of $\overline{|F|}$	$\Sigma\|F_{obs}\|$	$\Sigma\|F_{calc}\|$	$\Sigma\|F_o-F_c\|$	R
0.00 - 0.25	3675	3657	1162	0.32
0.25 - 0.50	25905	23858	2942	0.11
0.50 - 0.75	36203	35360	2333	0.06
0.75 - 1.00	35451	35278	1667	0.05
1.00 - 1.25	27937	28063	1035	0.04
1.25 - 1.50	28226	28451	1033	0.04
1.50 - 1.75	16052	16276	624	0.04
1.75 - 2.00	17025	17294	687	0.04
2.00 - 2.25	15257	15338	649	0.04
⩾2.25	82863	85056	3660	0.04

(iii) Against the Miller Indices:

h	R	k	R	ℓ	R
0	0.07	0	0.07	0	0.05
1	0.05	1	0.05	1	0.05
2	0.05	2	0.05	2	0.05
3	0.04	3	0.06	3	0.05
4	0.05	4	0.05	4	0.06
5	0.06	5	0.05	5	0.06
6	0.06	6	0.05	6	0.06
7	0.05	7	0.05	7	0.07
8	0.06	8	0.05	8	0.06
9	0.06	9	0.05	9	0.10
⩾10	0.06	⩾10	0.06		

TABLE 10

Oxygen and Carbon Atoms:

Final Fractional Co-ordinates and Estimated Standard Deviations.

Atom	x	ESD(x)	y	ESD(y)	z	ESD(z)
C(1)	0.04559	0.00026	0.16634	0.00017	0.35301	0.00045
C(2)	0.13071	0.00027	0.19085	0.00017	0.21988	0.00044
C(3)	0.24351	0.00026	0.18347	0.00017	0.30407	0.00045
C(4)	0.24681	0.00026	0.22974	0.00017	0.47344	0.00043
C(5)	0.15017	0.00025	0.21295	0.00017	0.59563	0.00043
C(6)	0.14004	0.00029	0.27063	0.00018	0.74292	0.00045
O(1)	0.07043	0.00017	0.09142	0.00012	0.39735	0.00031
O(2)	0.12701	0.00021	0.14719	0.00014	0.06354	0.00033
O(3)	0.32865	0.00021	0.21091	0.00015	0.19510	0.00037
O(4)	0.34171	0.00020	0.21523	0.00016	0.57356	0.00036
O(5)	0.04805	0.00018	0.21424	0.00012	0.50227	0.00032
O(6)	0.14786	0.00023	0.34549	0.00013	0.68414	0.00036
C(1')	0.48614	0.00025	0.44866	0.00018	0.51576	0.00042
C(2')	0.46520	0.00026	0.02565	0.00018	0.02730	0.00041
C(3')	0.44233	0.00027	0.06813	0.00018	0.85652	0.00043
C(4')	0.04158	0.00026	0.43097	0.00017	0.26249	0.00045
C(5')	0.40993	0.00025	0.49127	0.00017	0.78488	0.00043
C(6')	0.29910	0.00028	0.49468	0.00019	0.87503	0.00052
O(2')	0.36878	0.00021	0.01918	0.00015	0.13075	0.00031
O(3')	0.40781	0.00025	0.14190	0.00014	0.89829	0.00035
O(4')	0.01238	0.00021	0.40134	0.00014	0.43089	0.00034
O(5')	0.39239	0.00017	0.45513	0.00013	0.61846	0.00032
O(6')	0.26215	0.00021	0.42261	0.00014	0.92920	0.00035
O(W1)	0.42803	0.00025	0.34580	0.00017	0.09884	0.00047
O(W2)	0.33461	0.00022	0.00066	0.00015	0.47906	0.00034

TABLE 11

Oxygen and Carbon Atoms:

Final Anisotropic Thermal Vibration Parameters.

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
C(1)	0.00296	0.00121	0.00919	-0.00117	-0.00118	0.00009
C(2)	0.00370	0.00133	0.00711	0.00003	-0.00059	0.00022
C(3)	0.00305	0.00123	0.00787	-0.00024	0.00188	-0.00013
C(4)	0.00259	0.00138	0.00817	-0.00065	0.00025	-0.00045
C(5)	0.00292	0.00125	0.00786	-0.00017	0.00055	-0.00038
C(6)	0.00403	0.00145	0.00815	-0.00085	0.00000	-0.00048
O(1)	0.00242	0.00116	0.00823	-0.00039	0.00058	-0.00051
O(2)	0.00421	0.00204	0.00825	-0.00112	-0.00137	0.00069
O(3)	0.00424	0.00210	0.01147	-0.00244	0.00559	-0.00182
O(4)	0.00260	0.00296	0.00955	0.00085	-0.00124	-0.00028
O(5)	0.00266	0.00137	0.00866	-0.00158	-0.00053	0.00031
O(6)	0.00525	0.00133	0.01101	-0.00145	-0.00420	0.00016
C(1')	0.00270	0.00165	0.00589	-0.00144	-0.00152	0.00016
C(2')	0.00296	0.00178	0.00604	-0.00042	-0.00031	-0.00052
C(3')	0.00331	0.00162	0.00613	-0.00113	-0.00010	0.00073
C(4')	0.00320	0.00136	0.00808	0.00052	-0.00088	-0.00029
C(5')	0.00240	0.00143	0.00755	-0.00068	0.00054	0.00004
C(6')	0.00325	0.00171	0.01154	-0.00051	0.00316	-0.00040
O(2')	0.00383	0.00285	0.00534	-0.00035	0.00238	-0.00004
O(3')	0.00649	0.00179	0.00921	-0.00042	0.00372	0.00255
O(4')	0.00434	0.00193	0.00952	0.00339	-0.00425	-0.00099
O(5')	0.00204	0.00165	0.00878	-0.00151	0.00001	0.00022
O(6')	0.00413	0.00196	0.00988	-0.00003	0.00179	-0.00164
O(W1)	0.00518	0.00280	0.01790	0.00537	0.00150	-0.00034
O(W2)	0.00455	0.00247	0.00829	0.00143	-0.00206	0.00043

TABLE 12

Final Fractional Co-ordinates of the Hydrogen Atoms.

Atom	Bonded to	x	y	z
H(1)	C(1)	0.475	0.330	0.686
H(2)	C(2)	0.108	0.242	0.184
H(3)	C(3)	0.261	0.130	0.333
H(4)	C(4)	0.250	0.283	0.449
H(5)	C(5)	0.160	0.163	0.656
H(6)	C(6)	0.204	0.261	0.837
H(7)	C(6)	0.070	0.252	0.807
H(8)	O(2)	0.058	0.158	0.994
H(9)	O(3)	0.348	0.181	0.120
H(10)	O(4)	0.405	0.235	0.538
H(11)	O(6)	0.094	0.356	0.601
H(12)	C(1')	0.464	0.432	0.415
H(13)	C(2')	0.020	0.449	0.904
H(14)	C(3')	0.386	0.043	0.798
H(15)	C(4')	0.092	0.397	0.196
H(16)	C(5')	0.455	0.455	0.848
H(17)	C(6')	0.199	0.480	0.486
H(18)	C(6')	0.241	0.478	0.276
H(19)	O(2')	0.304	0.009	0.051
H(20)	O(3')	0.392	0.160	0.795
H(21)	O(4')	0.453	0.069	0.536
H(22)	O(6')	0.223	0.401	0.830
H(23)	O(W1)	0.402	0.302	0.134
H(24)	O(W1)	0.378	0.368	0.043
H(25)	O(W2)	0.152	0.045	0.996
H(26)	O(W2)	0.336	0.003	0.374

6. DISCUSSION OF THE STRUCTURE

The final structure is shown projected on to the (001) plane and the α,α-trehalose molecule alone is shown projected on to the (100) plane (figs 17 and 18). The molecules are held together by van der Waal's forces and by a complex network of hydrogen bonds which are listed below (Table 13) and represented diagramatically (fig 19). These twelve bonds utilise all the hydrogen atoms which are available for hydrogen bonding, i.e. all the hydroxyl groups in the structure.

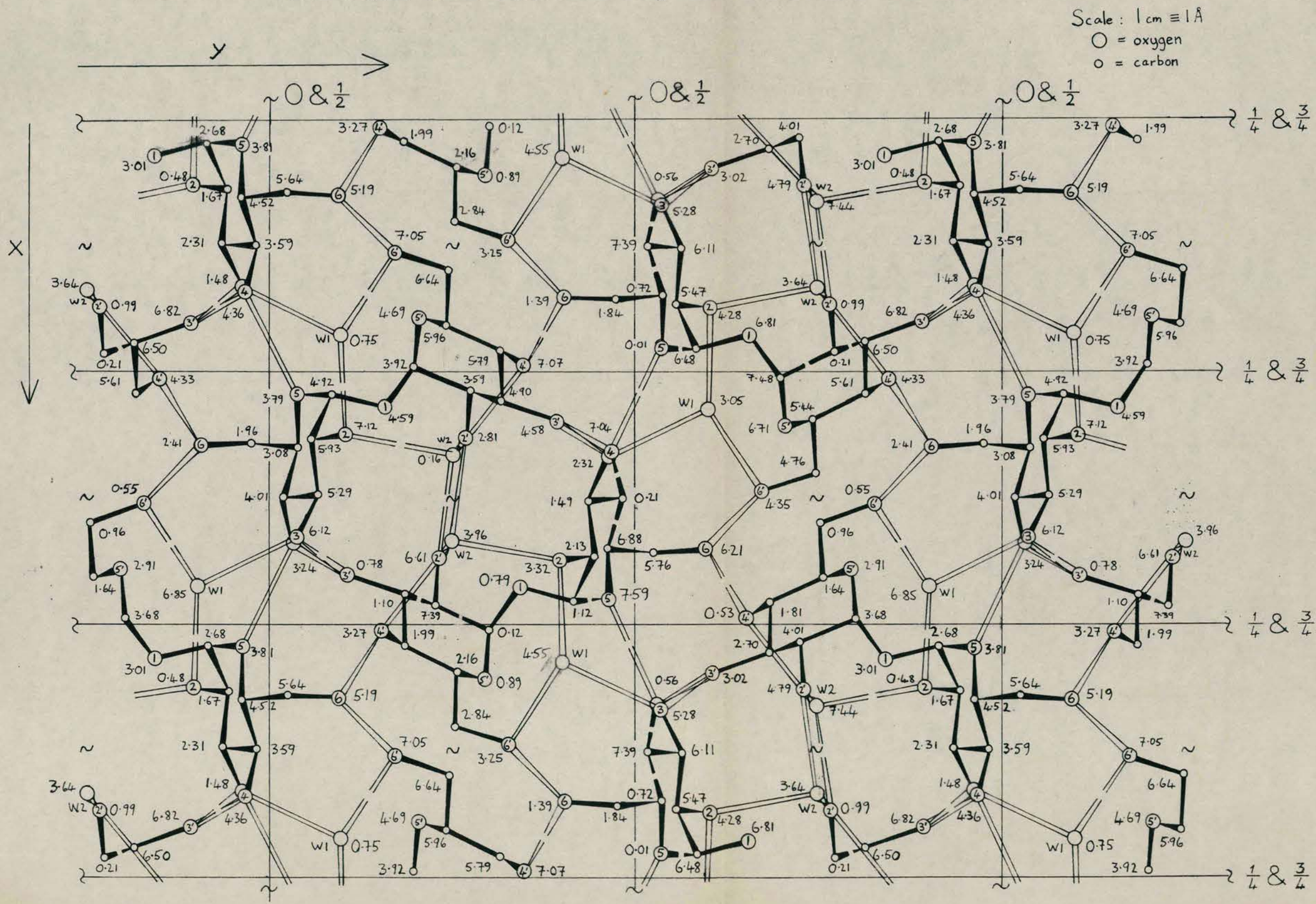
TABLE 13

The Hydrogen Bonds.

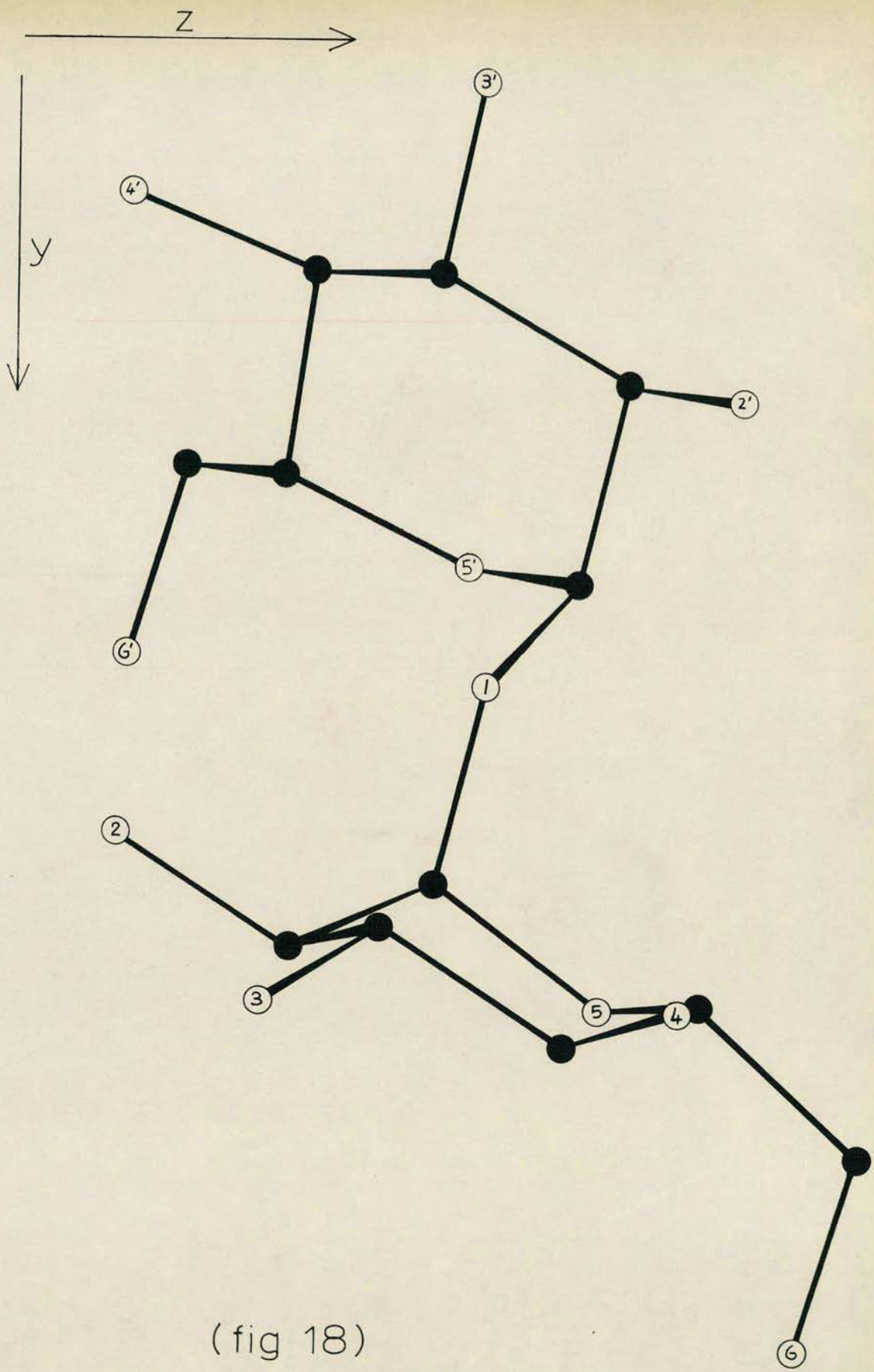
O —— H - - - - O			Bond Length	E.S.D.
O(2)	H(8)	O(W1)	2.732 Å	0.0041 Å
O(3)	H(9)	O(3')	2.747	0.0038
O(4)	H(10)	O(5)	2.880	0.0034
O(6)	H(11)	O(4')	2.729	0.0037
O(2')	H(19)	O(W2)	2.765	0.0037
O(3')	H(20)	O(4)	2.908	0.0038
O(4')	H(21)	O(W2)	2.876	0.0037
O(6')	H(22)	O(6)	2.706	0.0037
O(W1)	H(23)	O(3)	2.799	0.0041
O(W1)	H(24)	O(6')	2.769	0.0041
O(W2)	H(25)	O(2)	2.762	0.0037
O(W2)	H(26)	O(2')	2.699	0.0035

Fig (17)

The Final Structure Projected on to (001).

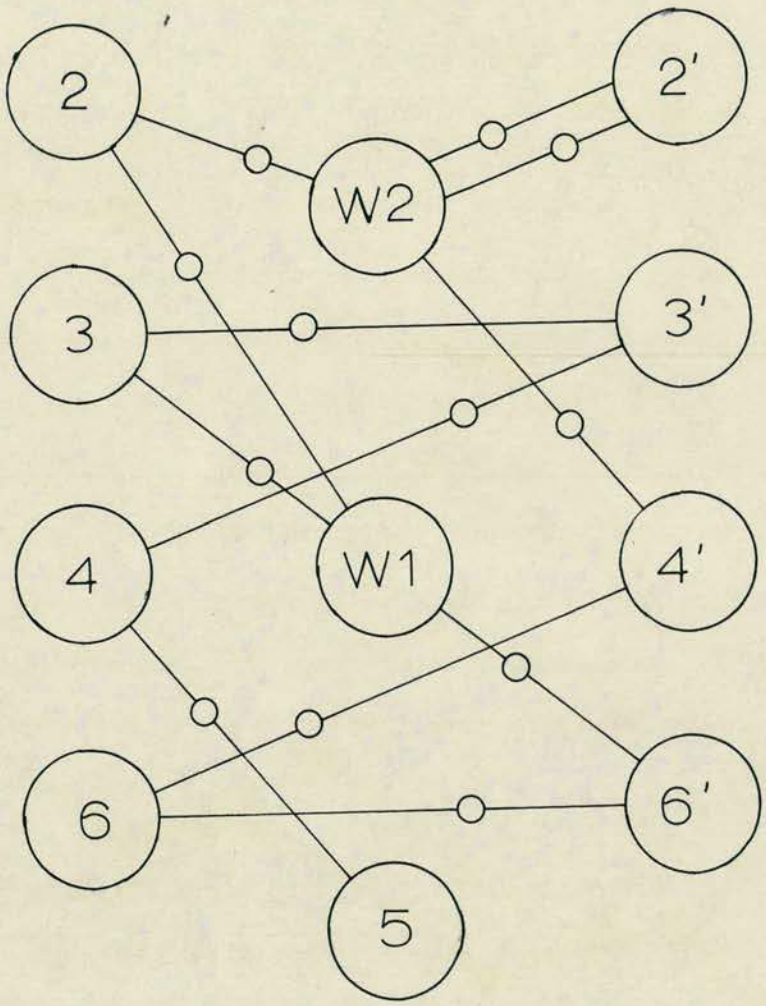


Projection on to (100).



(fig 18)

The Hydrogen Bonds.



o = hydrogen

= oxygen

(fig 19)

The only remaining short contact is one of 2.951 Å between atoms O(4) and O(4'). This is considerably longer than the longest of the hydrogen bonds. Nine of the hydrogen bonds are between 2.7 and 2.8 Å long and the three longer ones all involve either O(4) or O(4'). O(W1) is trigonally co-ordinate and O(W2) tetrahedrally, the latter being the acceptor in one of the longer hydrogen bonds. The observed thermal vibration is greater for O(W1) than for O(W2), as would be expected.

There is no inter-residue bond joining, e.g. O(2) to O(5'). This was also found in the case of raffinose (H. M. Berman, 1970) which again has about one molecule of water of crystallisation per sugar residue. Other oligosaccharide structures have always included such a bond. The glucosidic oxygen atom does not function as an acceptor in a hydrogen bond; this appears to be a general rule (M. Sundralingam, 1968) although no clear reason why this should be so has emerged. The acetal oxygen atom in one residue, O(5), participates in the hydrogen bonding whereas the other, O(5'), does not. The hydrogen bond concerned, O(4) - H(10) - - - O(5), is rather long at 2.88 Å; this effect has been noted before (e.g. T. R. R. McDonald, 1950).

The bond lengths and their estimated standard deviations (Table 14) and bond angles and their estimated standard deviations (Table 15) are shown below. A comparison of the bond lengths calculated in this study with those obtained in the independent structure determinations is given later (Appendix III). The molecule was found to be in the expected conformation, with the pyranoid rings in the "chair" form and all the substituents to the rings, except O(1), in equatorial positions.

TABLE 14

Final Bond Lengths and their Estimated Standard Deviations.

Atoms	Length	E.S.D.	Atoms	Length	E.S.D.
C(1) - C(2)	1.516 Å	0.0047 Å	C(1') - C(2')	1.536 Å	0.0045 Å
C(2) - C(3)	1.527	0.0046	C(2') - C(3')	1.529	0.0045
C(3) - C(4)	1.530	0.0046	C(3') - C(4')	1.514	0.0046
C(4) - C(5)	1.533	0.0045	C(4') - C(5')	1.522	0.0043
C(5) - C(6)	1.527	0.0046	C(5') - C(6')	1.520	0.0047
C(1) - O(1)	1.415	0.0038	C(1') - O(1)	1.419	0.0038
C(1) - O(5)	1.421	0.0040	C(1') - O(5')	1.392	0.0038
C(5) - O(5)	1.437	0.0038	C(5') - O(5')	1.436	0.0040
C(2) - O(2)	1.422	0.0041	C(2') - O(2')	1.422	0.0040
C(3) - O(3)	1.418	0.0042	C(3') - O(3')	1.421	0.0041
C(4) - O(4)	1.412	0.0041	C(4') - O(4')	1.430	0.0042
C(6) - O(6)	1.415	0.0040	C(6') - O(6')	1.427	0.0043
C(1) - H(1)	0.919	0.057	C(1') - H(12)	0.867	0.064
C(2) - H(2)	0.989	0.057	C(2') - H(13)	0.961	0.060
C(3) - H(3)	0.997	0.057	C(3') - H(14)	0.933	0.059
C(4) - H(4)	0.976	0.057	C(4') - H(15)	0.999	0.059
C(5) - H(5)	1.005	0.058	C(5') - H(16)	0.975	0.059
C(6) - H(6)	1.074	0.061	C(6') - H(17)	0.956	0.058
C(6) - H(7)	1.036	0.062	C(6') - H(18)	1.022	0.059
O(2) - H(8)	1.012	0.059	O(2') - H(19)	1.012	0.059
O(3) - H(9)	0.819	0.062	O(3') - H(20)	0.865	0.064
O(4) - H(10)	0.894	0.061	O(4') - H(21)	0.935	0.057
O(6) - H(11)	0.931	0.061	O(6') - H(22)	0.975	0.058
O(W1) - H(23)	0.879	0.059	O(W2) - H(25)	0.837	0.058
O(W2) - H(24)	0.842	0.059	O(W2) - H(26)	0.802	0.061

TABLE 15

Final Bond Angles and their Estimated Standard Deviations.

	Angle	E.S.D.		Angle	E.S.D.
O(5) C(1) O(1)	112.12°	0.250°	O(5') C(1') O(1)	112.34°	0.250°
O(5) C(1) C(2)	110.07	0.256	O(5') C(1') C(2')	111.36	0.254
O(1) C(1) C(2)	106.57	0.252	O(1) C(1') C(2')	105.70	0.245
C(1) C(2) O(2)	112.10	0.263	C(1') C(2') O(2')	111.48	0.256
C(1) C(2) C(3)	108.44	0.261	C(1') C(2') C(3')	109.63	0.258
O(2) C(2) C(3)	109.34	0.259	O(2') C(2') C(3')	110.94	0.258
C(2) C(3) O(3)	112.92	0.265	C(2') C(3') O(3')	109.05	0.263
C(2) C(3) C(4)	109.22	0.260	C(2') C(3') C(4')	111.42	0.265
O(3) C(3) C(4)	106.51	0.257	O(3') C(3') C(4')	111.20	0.267
C(3) C(4) O(4)	112.03	0.261	C(3') C(4') O(4')	109.74	0.260
C(3) C(4) C(5)	112.50	0.259	C(3') C(4') C(5')	111.69	0.264
O(4) C(4) C(5)	105.78	0.253	O(4') C(4') C(5')	109.65	0.257
C(4) C(5) C(6)	111.95	0.260	C(4') C(5') C(6')	111.18	0.266
C(4) C(5) O(5)	111.63	0.249	C(4') C(5') O(5')	111.80	0.251
C(6) C(5) O(5)	106.27	0.249	C(6') C(5') O(5')	106.34	0.254
C(5) O(5) C(1)	113.73	0.235	C(5') O(5') C(1')	114.06	0.238
C(5) C(6) O(6)	113.76	0.273	C(5') C(6') O(6')	112.10	0.280
C(1) O(1) C(1')	115.68	0.236			

Bonds involving hydrogen atoms:

Bonds	Number	E.S.D.	Range
X - X - H	46	~3.5°	97 - 121°
H - X - H	4	~5°	101 - 116°

The angle at the glycosidic linkage was found to be 115.7° (three estimated standard deviations = 0.7°). This is similar to other results quoted in the literature (Table 16). Since this angle is greater than the tetrahedral value of 109°28' it appears that the mutual repulsion of the two groups on either side of the glycosidic oxygen atom is a larger effect than the repulsion between the two lone pairs of electrons attached to it.

TABLE 16

Bond Angles at Glycosidic Linkages.

Sugar	Angle	Reference
Sucrose	114°	G. M. Brown and H. A. Levy, 1963.
Cellobiose	117.5°	R. A. Jacobson, J. A. Wunderlich and W. N. Lipscomb, 1961.
"	116.7°	C. J. Brown, 1966.
"	116.1°	S. S. C. Chu and G. A. Jeffrey, 1968.
Lactose	118.3°	H. N. Hansen, 1970.
Raffinose - sucrose	122°	H. M. Berman, 1970.
melibiose	111°	
Methyl-α-D-mannopyranoside	113.4°	B. M. Gatehouse and B. J. Poppleton, 1970.
Methyl-α-D-glucopyranoside	113.0°	H. M. Berman and S. H. Kim, 1968.

The exo-anomeric effect (A. J. de Hoog, H. R. Buys, C. Altona and E. Havinga, 1969) often dominates the conformation about C(1) - O(1), and does so here for both linkages. The rotations about the C(1) - O(1) and C(1') - O(1) bonds are described by the two dihedral angles:

$$C(1) - O(1) - C(1') - C(4') = 120.7^{\circ}$$
$$C(1') - O(1) - C(1) - C(4) = 134.7^{\circ}$$

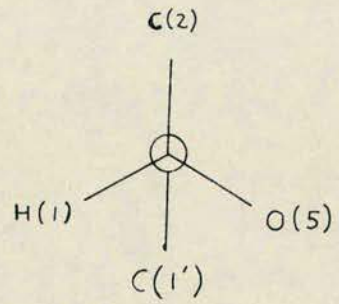
Newman projections down these two bonds are shown (fig 20), from which it may be seen that the above dihedral angles must be roughly 120° in order to minimise the interactions between the atoms bonded to C(1) or C(1') and the atom and two lone pairs of electrons on O(1).

The bond lengths and angles involving hydrogen atoms were calculated from the refined hydrogen atom positions. Their values are not reliable but are significant in so far as they agree reasonably well with the expected geometry. This suggested that the other refined parameters were likely to be accurately determined. It is with the oxygen and carbon atoms that the remainder of this discussion is concerned.

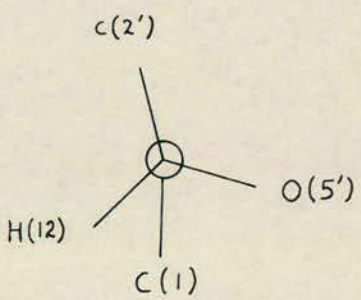
For an α-linkage in a glucopyranose ring, the C(1) - O(5) bond is usually shorter than average whereas the C(1) - O(1) bond is of more nearly normal length; the opposite is true for β-linkages (M. Sundralingam, 1968). In this respect it is clear that an unsubstituted or methylated O(1) atom behaves differently from one linked to another sugar ring. Few structures of glucosidic sugars have been determined accurately so an existing summary (H. M. Berman and S. H. Kim, 1968) may now be usefully extended (Table 17).

Newman Projections.

(i) Down C(1) - O(1):



(ii) Down C(1') - O(1):



(fig 20)

TABLE 17

Bond Length Variations in Glucosidic Sugars.

$\overline{C-C}$ Range	$\overline{C-OH}$ Range	3σ	Bond Length Variation C5 - O5 - C1 - O1 - R				Ref
1.523Å (24)	1.417Å (12)	9	+10	+9	-28	H	1
1.519 (25)	1.424 (13)	12	+10	-10	-13	CH_3	2
1.524 (19)	1.428 (12)	22	+12	-20	-12	glu	3
1.525 (14)	1.418 (10)	9	+18	-10	+2	fruc	4
1.519 (18)	1.424 (11)	12	+13	+9	-41	H	5
1.525 (22)	1.421 (18)	13	+16	0	-6	glu	6
			+15	-29*	-2	glu	7

The values of the ranges, 3σ and the variations are in 10^{-3}Å.

*The two independent sets of bond lengths have this figure about -13; none of the other figures quoted are much different in the three sets of results.

Ref 1: α-D-glucose (G. M. Brown and H. A. Levy, 1965)

2: Methyl-α-D-glucopyranoside (H. M. Berman and S. H. Kim, 1968)

3: β-methyl-β-D-maltopyranoside (S. S. C. Chu and G. A. Jeffrey, 1967)

4: Sucrose (G. M. Brown and H. A. Levy, 1963)

5: β-D-glucose (S. S. C. Chu and G. A. Jeffrey, 1968)

6 and 7 refer to rings one and two of the present work.

The two compounds which contain axial C(1) - O(1) bonds, i.e. β-methyl-β-D-maltopyranoside and sucrose, both closely resemble the present set of results. Overall, the C(5) - O(5) bond is considerably longer than average, the C(1) - O(5) bond is shorter than average and the C(1) - O(1) bond is very slightly shorter than average.

The most striking feature in the list of bond lengths (Table 14) is perhaps the large difference, of about 7.4 estimated standard deviations, between the C(1) - O(5) and C(1') - O(5') bonds. Although the results of the two independent structure determinations do reduce the absolute difference, its significance remains very high at about six standard deviations for the most accurate set of data. The explanation of this effect would appear to be that O(5) takes part in a hydrogen bond whereas O(5') does not. Crystal packing has been responsible for a change of bond length comparable in magnitude to the changes brought about by internal effects in the molecule.

Examination of the bond angles in each ring (Table 15) reveals several significant differences, including one of no less than eighteen estimated standard deviations. These large differences relate to the geometry about atoms C(3) and C(4) compared to C(3') and C(4') and in both cases are largest for the bond angles involving the substituent oxygen atoms. These differences must also be explained in terms of the different packing of the two sets of atoms causing different distortions from the positions the atoms would adopt in an isolated molecule. In this context it should be remembered that there was a short contact between atoms O(4) and O(4') which may have contributed to these distortions.

The two pyranoid rings have closely similar internal bond angles. The average internal bond angles in the two rings are 110.9° and 111.7° respectively, which are rather greater than the corresponding values for other accurately determined glucose rings. The largest angle in both rings is about 114° at the acetal oxygen atom and the smallest angles are about 109° at C(2) and C(2'). These values follow a similar pattern to those in other glucose rings (Table 18, p.78). The rings are rather flatter than they would have been had the bond angles been exactly tetrahedral.

In conclusion, the two crystallographically unrelated glucose rings in the α,α-trehalose structure were shown to be closely similar. The effect of the different crystal packing of the two rings was chiefly evidenced by distortion of the bond angles to some of the substituent atoms, although one bond length in the ring was significantly altered. The approximate molecular shape of glucose, obtained by averaging the two rings in this structure, could be applied to studies of polysaccharides with little error. The exact geometry of any glucose residue does, however, depend on its environment. It is hoped that one of the uses of the present work may be to indicate the limits of this approximation.

TABLE 18

The Bond Angles in Various Glucose Rings.

$\widehat{C(1)}$	$\widehat{C(2)}$	$\widehat{C(3)}$	$\widehat{C(4)}$	$\widehat{C(5)}$	$\widehat{O(5)}$	Mean	Ref
106.9°	109.8°	109.1°	110.8°	110.2°	114.0°	110.1°	1
108.5	112.1	110.5	109.8	107.6	112.7	110.2	2
108.3	108.3	109.5	111.0	110.5	112.4	110.0	3a
109.3	110.0	111.8	112.3	109.2	113.5	111.0	3b
107.8	111.1	106.1	109.1	108.8	114.7	109.6	4a
110.3	109.8	110.7	111.0	108.2	111.5	110.3	4b
110.1	108.4	109.2	112.5	111.6	113.7	110.9	5a
111.4	109.6	111.4	111.7	111.8	114.1	111.7	5b
109.1	109.9	109.8	111.0	109.8	113.3	110.5	(Mean)

Ref 1: Methyl-α-D-glucopyranoside (H. M. Berman and S. H. Kim, 1968).

2: β-D-glucose (S. S. C. Chu and G. A. Jeffrey, 1968).

3a and b: Cellobiose (ibid.); a and b refer to the rings with linkages at C(1) and C(4') respectively.

4a and b: β-methyl-β-D-maltopyranoside (S. S. C. Chu and G. A. Jeffrey, 1967); a and b refer to the rings with linkages at C(1) and C(4') respectively.

5a and b: α,α-trehalose, rings one and two respectively.

SECTION TWO: DIETHYLIDENE TREHALOSE MONOHYDRATE

1. PRELIMINARY INVESTIGATION

(a) Physical Examination.

Crystals were again kindly supplied by Dr. Birch. They were in the form of colourless needles and showed clear extinctions when viewed between crossed polarisers. They were too small for any piezo-electric effect to be detected. Solutions of the material, however, do exhibit optical rotation (G. G. Birch, 1966) so that only one stereo-isomer must be present. The crystals must therefore belong to a non-centrosymmetric space group.

A smallish, apparently perfect, crystal was now selected with the aid of the microscope. When this crystal was broken into fragments it was found to be very much softer than α,α-trehalose dihydrate. This was assumed to be due to the fact that only six hydrogen bonds are possible per molecule of diethylidene trehalose compared to twelve in the case of α,α-trehalose. The density was measured by flotation in a mixture of iodomethane and benzene. It was found to be 1.452 $g.cm^{-3}$, in reasonable agreement with an earlier value of 1.42 $g.cm^{-3}$ (G. G. Birch, 1965b).

(b) Space Group Determination.

One of the crystals was now mounted so that it rotated about an axis parallel to its elongated direction. Photographs were taken using the 10 cm diameter normal beam Weissenberg camera. An oscillation photograph showed that this direction corresponded to some kind of two-fold symmetry.

A zero-layer Weissenberg photograph ~~showed that there were~~ suggested two possible axes perpendicular to this direction, mutually inclined at about 82.8°. Thus it appeared that the symmetry was monoclinic.

Further photographs were obtained with the crystal rotating about the other two axes. These confirmed that the crystal was of monoclinic symmetry and showed that the only systematically absent reflections were I(0k0) when k was odd, with b defined as the unique axis. This information was consistent with only one space group, $P2_1$, number 4, second setting (International Tables, vol I). An approximate set of cell dimensions was obtained from the oscillation photographs:

$$a = 11.1 \text{ Å}$$
$$b = 8.3$$
$$c = 9.9$$

From these results it was calculated that the number of molecules of diethylidene trehalose in the unit cell was two, i.e. the asymmetric unit of the structure contained one molecule.

(c) Accurate Cell Dimensions.

Only two of the three zero-layer Weissenberg photographs, i.e. those showing I(hk0) and I(h0ℓ), contained sufficient strong high angle reflections to allow accurate calculation of the cell dimensions involved. The (hk0) reflections were treated first. For them the reciprocal lattice was orthogonal, so that a graphical treatment like that described above (p. 13) was possible. From the photograph the $\sin^2\theta$ values were obtained for both the K_{α_1} and K_{α_2} components of each reflection. An accurate value

of the (a^*/b^*) ratio was deduced and hence, by extrapolation to $\sin^2\theta = 1$, it was found that:

$$b = 8.435 \text{ Å}$$

$$a.\sin\beta^* = 11.176$$

For the $(h0\ell)$ reflections the reciprocal lattice is not orthogonal and the spacing is given by:

$$d^2 = h^2.(a^*)^2 + \ell^2.(c^*)^2 + 2.\underline{h}.\underline{\ell}.a^*.c^*.\cos\beta^*$$

A value of c^* may be obtained from the reflections with low h if the other two unknowns, a^* and $\cos\beta^*$, are given approximate values. A value of a^* may be obtained in a similar way. The remaining reflections may be used to obtain a better value of $\cos\beta^*$, using the values of a^* and c^* deduced.

A program was written in the Atlas Autocode language for the KDF9 computer to refine the approximate cell parameters obtained above. The input data consisted of the reflections with their $\sin^2\theta$ values, a range of values of $\cos\beta^*$ and a range of values of the ratio (c^*/a^*). For each pair of values of $\cos\beta^*$ and (c^*/a^*), a^* and c^* were plotted against $\sin^2\theta$. The approximate form of the method of least squares (p.14, above) was used to extrapolate the best straight line to $\sin^2\theta = 1$ for both and to calculate estimated standard deviations in both extrapolated values. The best values of $\cos\beta^*$ and (c^*/a^*) were those which yielded the lowest standard deviations. The use of reasonably accurate starting values ensured that only one minimum appeared during the refinement. For the correct (c^*/a^*) ratio the minimum estimated standard deviations in a^* and c^*, i.e. $\sigma(a^*)$ and $\sigma(c^*)$, should occur at the same value of $\cos\beta^*$.

If the ratio is incorrect then, in general, these two minima occur at different $\cos\beta^*$ values.

The refinement was completed in three cycles, using progressively finer increments in the variables and reducing their ranges. The results obtained for Cu K_{α_1} radiation (λ = 1.5405 Å) were:

$$a^* = 0.13782 \qquad \sigma(a^*) = 0.000023$$
$$c^* = 0.15535 \qquad \sigma(c^*) = 0.000026$$
$$\cos\beta^* = 0.13192$$

There was no easy way of calculating a standard deviation of $\cos\beta^*$ so instead it was noted that when $\cos\beta^*$ increased to 0.1340, $\sigma(a^*)$ and $\sigma(c^*)$ increased three times. This was used to fix the estimated error in β^*. The value of $a.\sin\beta^*$ was thus found to be 11.177 Å which was in excellent agreement with the previous value of 11.176 Å.

The final values of the cell parameters and three times the estimated standard deviation in each were as follows:

$$a = 11.276 \ (0.008) \text{ Å}$$
$$b = 8.435 \ (0.004)$$
$$c = 10.004 \ (0.007)$$
$$\beta = 97.58^\circ \ (0.12^\circ)$$

Assuming that the material investigated was a monohydrate, in accordance with the results of micro-analysis (G. G. Birch, 1966), then the density was calculated to be 1.445 $g.cm^{-3}$; observed density = 1.452 $g.cm^{-3}$.

2. THE INTENSITY DATA

(a) The Collection of the Intensity Data.

Only two or three of the crystals available were large enough to permit an attempt to be made to grind spheres from them. The crystal fragment was generally reduced to powder during the grinding process. Two spheres which were ground successfully both broke up whilst they were being aligned. It was therefore decided to use cylindrical specimens. A crystal of approximately the desired shape was rolled between two moist sheets of filter paper in order to round off its corners. The resulting specimen was slightly elliptical in cross-section. A separate cylinder was needed in order to take photographs with the crystal rotating about a different axis. Accordingly, the largest remaining single crystal was cut with a razor blade in order to obtain, after rounding it off, a cylinder with its axis parallel to the second longest edge of the original crystal. It was correctly anticipated that this would be parallel to c.

The 5.73 cm diameter camera was now used to obtain equi-inclination Weissenberg photographs of the layers $k = 0$ to $k = 6$ using the first crystal and $\ell = 0$ to $\ell = 5$ with the second. Multiple film packs were used. For the higher layers packs of five films were used with only one exposure instead of two. An intensity strip was prepared with each crystal. The intensities of those spots on each film which fell within the range of the appropriate intensity strip were now measured.

It was found that the observed effect of spot shape variation was much more severe with these cylindrical crystals than it had been with the spherical crystals of α,α-trehalose. This was presumed to be because

the shape which the eye had to integrate was much less regular. In consequence, frequent checks were made to ensure that the recorded value of an intensity did not depend on whether the extended or contracted form of the spot had been measured. When there was a difference between the two forms of a spot then for all the intensities measured on that portion of the film the harmonic mean of the two values was taken to be correct. For the photographs taken of the second crystal, only those intensities for which h was positive could be measured accurately. This was probably due to irregularities in the crystal shape. The data with h negative were rejected and some doubt was cast on the accuracy of the rest of the data.

(b) The Correction and Scaling of the Intensity Data.

The ratio of intensities between two adjacent films from the same pack lay in the range 2.8 to 3.0. Lorentz, polarisation and absorption corrections for cylindrical crystals (International Tables, vol II) were now applied to the separate layers of data. These layers of data, corresponding to the film packs, were now scaled together. For this purpose the weakest and strongest intensities and those at high angles were all weighted down.

Altogether there were 1,818 observed reflections and 164 non-systematic absences, making a total of 1,982 reflections in the intensity data list. The increased number of non-systematic absences compared to the data for α,α-trehalose was due partly to the smaller crystal size and partly to the fact that there was less duplication of measurement. There were some 2,300 reflections theoretically accessible with Cu K_α radiation, so that about 86% of the accessible reflections were measured, although some of them were estimated to be of zero intensity.

An estimation of the accuracy of the data was obtained from those intensities which had been measured twice. The results shown (Table 19) appear to be about as good as those for α,α-trehalose (Table 1). It was, however, known that this assessment of the diethylidene trehalose data was considerably over-optimistic. In the first place, most of the data for α,α-trehalose had been measured at least twice, whereas in the present case only some of the intensities had been measured twice, and those same intensities had been used for scaling purposes. In the second place, the fact that some of the observed data were rejected must obviously cast some doubt on the remainder. A further drawback of this set of data is that many of the high angle reflections were missed. There was, therefore, a lower value of the root mean square reciprocal radius for diethylidene trehalose than for α,α-trehalose, so that even if refinement proceeded to the same final residual in both cases, the accuracy of the final parameters would be less for diethylidene trehalose.

(c) Intensity Statistics.

A Wilson plot was again used in order to find the mean temperature factor for all the carbon and oxygen atoms in the unit cell and the scale factor needed to reduce the intensities to an absolute scale. The contributions of the hydrogen atoms were ignored. The mean temperature was found to be 2.12 $\mathring{A}^2$, rather less than the corresponding value of 2.3 $\mathring{A}^2$ found for α,α-trehalose. This was rather surprising, since it was known that the hydrogen bonding between molecules would be weaker in the present case. It was therefore expected that the thermal vibration would be greater, not less. It was noted, however, that this could be due, in part at least,

TABLE 19

Accuracy of the Diethylidene Trehalose Intensity Data.

Range of I	ND	σ(F)
1 - 9	114	45.8%
10 - 29	192	13.8
30 - 59	170	6.8
60 - 99	106	6.7
100 - 299	230	5.1
300 - 599	104	4.3
600 - 999	60	5.4
1000 - 1999	22	3.5
≥2000	22	7.0

ND represents the number of duplicated measurements.

****

to secondary extinction effects. The crystals were so soft that thermal shock treatment would have been disastrous, so nothing at all was done to minimise any such effects. Since the program which was used divided the data into twenty equal ranges of $\sin^2\theta$ (rather than the more correct $\sin^3\theta$) the three or four lowest points in the Wilson plot were dominated by the few largest intensities. If these suffered badly from extinction then the effect would be to reduce the calculated temperature factor significantly. The scale factor, which was found to be 0.76, required to convert the data to an absolute scale would be too low.

N(Z) distributions were calculated for all the intensity data and separately for the (0kℓ), (h0ℓ) and (hk0) sets of projection data. These results, which are shown immediately below (Table 20), clearly indicated that only the (h0ℓ) data constituted a centrosymmetric zone, in accordance with the known space group, $P2_1$.

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TABLE 20

The N(Z) Test for Diethylidene Trehalose.

	Theoretical		Observed	N(Z)		
Z	Centro	Non	(hkℓ)	(0kℓ)	(h0ℓ)	(hk0)
0.1	0.248	0.095	0.13	0.12	0.29	0.18
0.2	0.345	0.181	0.22	0.20	0.35	0.24
0.3	0.419	0.259	0.31	0.33	0.44	0.30
0.4	0.474	0.330	0.39	0.37	0.48	0.33
0.5	0.520	0.393	0.46	0.47	0.52	0.38
0.6	0.561	0.451	0.51	0.51	0.56	0.42
0.7	0.597	0.503	0.56	0.59	0.59	0.45
0.8	0.629	0.551	0.60	0.64	0.62	0.51
0.9	0.657	0.593	0.64	0.65	0.65	0.56
1.0	0.683	0.632	0.67	0.68	0.67	0.59

3. THE PATTERSON APPROACH

(a) The Orientations of the Rings.

A three-dimensional Patterson summation was computed with very modest sharpening of the coefficients used. Allowance was made for part of the thermal vibration by means of a temperature factor of $B = 1$ Å^2, i.e. $2B = 2$ Å^2, but the reduction of intensities due to the atomic formfactor contribution was ignored. Intensities at very high values of $\sin^2\theta$ were thus weighted up by a factor of about 3. The spacings between grid points on the map were, in each direction, about 0.3 Å. The map generated was not only printed out in the usual way, but was also written on to magnetic tape by the computer, so that it would be available for the production of minimum function maps. This possible use of the Patterson map was the reason for applying such modest sharpening.

This first map was, of course, of very low resolution, so it was later decided to compute a second, sharper map. For this purpose the observed intensities were divided by the square of the atomic formfactor of nitrogen. This gave a close approximation to the appropriate average of the formfactors of carbon and oxygen. The hydrogen atoms were ignored. A temperature factor contribution of $2B = 3$ Å^2 was used. This degree of sharpening was almost, but not quite, equivalent to the point atom at rest approximation. The slight safety margin ensured that the highest angle intensities, which were not measured as accurately as the rest of the data, would not be able to produce large spurious features in the map.

It seemed probable, on stereochemical grounds, that for both halves of the molecule the ring closed by the ethylidene group would be of the "chair" form, parallel to the glucopyranoid ring, and that the methyl group would constitute an equatorial substituent to this new ring. For each double ring, i.e. 4,6-O-ethylidene glucosyl group, all of the bonds must then lie parallel to C(1) - C(2) , C(2) - C(3) or C(3) - C(4) with the sole exception of the glucosidic linkage. If only twenty-four large peaks lay at about 1.5 Å from the origin of the Patterson map then the suggested conformation would be confirmed, and the ring orientations deduced. These twenty-four peaks correspond to six peaks in the asymmetric unit of the Patterson map.

The three-dimensional Patterson summations yielded some rather disturbing information, for only twelve 1.5 Å vectors could be located, corresponding to only one ring orientation. A ball and spoke model of the peaks 1.5 and 2.5 Å removed from the origin of the Patterson maps was made. Comparison of this with a model of the molecule suggested that the explanation of this dearth of peaks was that the orientations of the two halves of the molecule were approximately related by a mirror plane parallel to (010). Thus the vectors from the two halves of the molecule were accidentally superimposed. It would have been straightforward to identify two separate sets of vectors in a Patterson synthesis with symmetry P2/m; the accidental superimposition of the two sets was unfortunate, since it made the task of obtaining more exact orientations very difficult.

More accurate orientations were deduced by selecting a set of three 2.5 Å vectors, say $\underline{p}$, $\underline{q}$ and $\underline{r}$ with the condition that $\underline{p} + \underline{q} + \underline{r} = 0$,

which fitted the observed peaks. These vectors were chosen so that the two sets were as different as possible, consistent with obtaining a good fit with the appropriate peaks in the map. The 1.5 Å vectors served to eliminate the ambiguity whereby two different ring orientations give the same set of 2.5 Å vectors, but they were of no use in refining the approximate orientations. This was done by considering all the vectors in each half of the molecule.

The long direction of each double ring was established by considering that the 2.5 Å vector parallel to it should be weighted eight times, compared to the others which should be weighted six times. The 2.5 Å vector corresponding to the largest peak was therefore the logical first choice. Parallel to that vector lies a 5 Å vector joining atoms on opposite sides of the double ring, and this should be weighted four times. The identification of this peak established the long direction of both halves of the molecule. It was now possible to work out positions for other peaks in the Patterson map and to use the accumulated results to refine the orientations further. The relative positions of ten atoms in each double ring are shown below (Table 21).

It was found that these orientations were quite accurate, the largest departures from the corresponding values calculated from the final refined atomic co-ordinates being about 0.2 Å. These errors were generally due to the inadequate resolution of the Patterson maps. The orientations A and B were consequently more nearly exact mirror images than in the final structure; this error was not unexpected. The double ring which is subsequently referred to as the first half of the molecule was found to lie in orientation A and the second half in orientation B.

TABLE 21

The Orientations of the Double Rings.

Atom	x_A	y_A	z_A	x_B	y_B	z_B
1	.000	.000	.000	.000	.000	.000
2	.000	.000	.143	.000	.017	.138
3	.100	.060	.218	.108	.040	.213
4	.100	.060	.358	.108	.057	.350
5	.200	.117	.433	.213	.077	.425
6	.250	.250	.383	.288	-.040	.400
7	.250	.250	.243	.288	-.057	.263
8	.150	.193	.168	.183	-.077	.188
9	.150	.193	.025	.183	-.093	.050
10	.050	.133	-.050	.075	-.117	-.025

****

(b) The Approximate Solution of the Structure.

Consideration of a model showed that the only way in which the two halves of the molecule could adopt the orientations established above was in an arrangement which, projected on to (010), was closely linear. The projection of the molecule had to be inclined at about 30° to c and 70° to a. It was thought that a molecule extended in this fashion could only be fitted into the unit cell if the glucosidic linkage were located at roughly the position ($x=\frac{1}{4}, z=\frac{1}{2}$), or its equivalent, so that it lay half way between two screw axes. In that case the two ethylidene groups would

lie close to screw axes, so that strong van der Waal's forces would exist between each ethylidene group and the two others related to it by the screw symmetry. Since in three dimensions there were considerable ambiguities concerning the orientations which would have to be resolved, it was decided to attempt to obtain a two-dimensional solution of the structure in the (010) projection first.

Since the ring orientations were known, it was possible to superimpose a plan of each double ring, on a scale twice that of the map, on the Harker section. Despite knowing the approximate position of the molecule in the unit cell, this procedure failed to establish the location of the double rings. The Harker section maps from both the three-dimensional Patterson summations were too complex to be interpreted, due to the very large number of vectors which accidentally fell close to $y = \frac{1}{2}$. The resolution of the maps, one of which is shown (fig 21), was in any case inadequate. A comparison of the final atomic positions with the Harker section peaks is shown.

Two Patterson syntheses were computed for the projection on to (010). The only sharpening applied to the coefficients for the first summation (fig 22) consisted of a temperature factor of $B = 1$ Å^2 (i.e. $2B = 2$ Å^2). For the second summation (fig 23) the point atom at rest approximation was assumed. Each double ring contains three principal centres of symmetry, for eight atoms are approximately centrosymmetrically disposed about the centre of each ring, and ten about the mid-point of the C(4) - C(5) bond. These three points are equally spaced, 1.25 Å apart, along a straight line parallel to the 5 Å vector of the double ring. In the

The Harker Section $P(x,\frac{1}{2},z)$

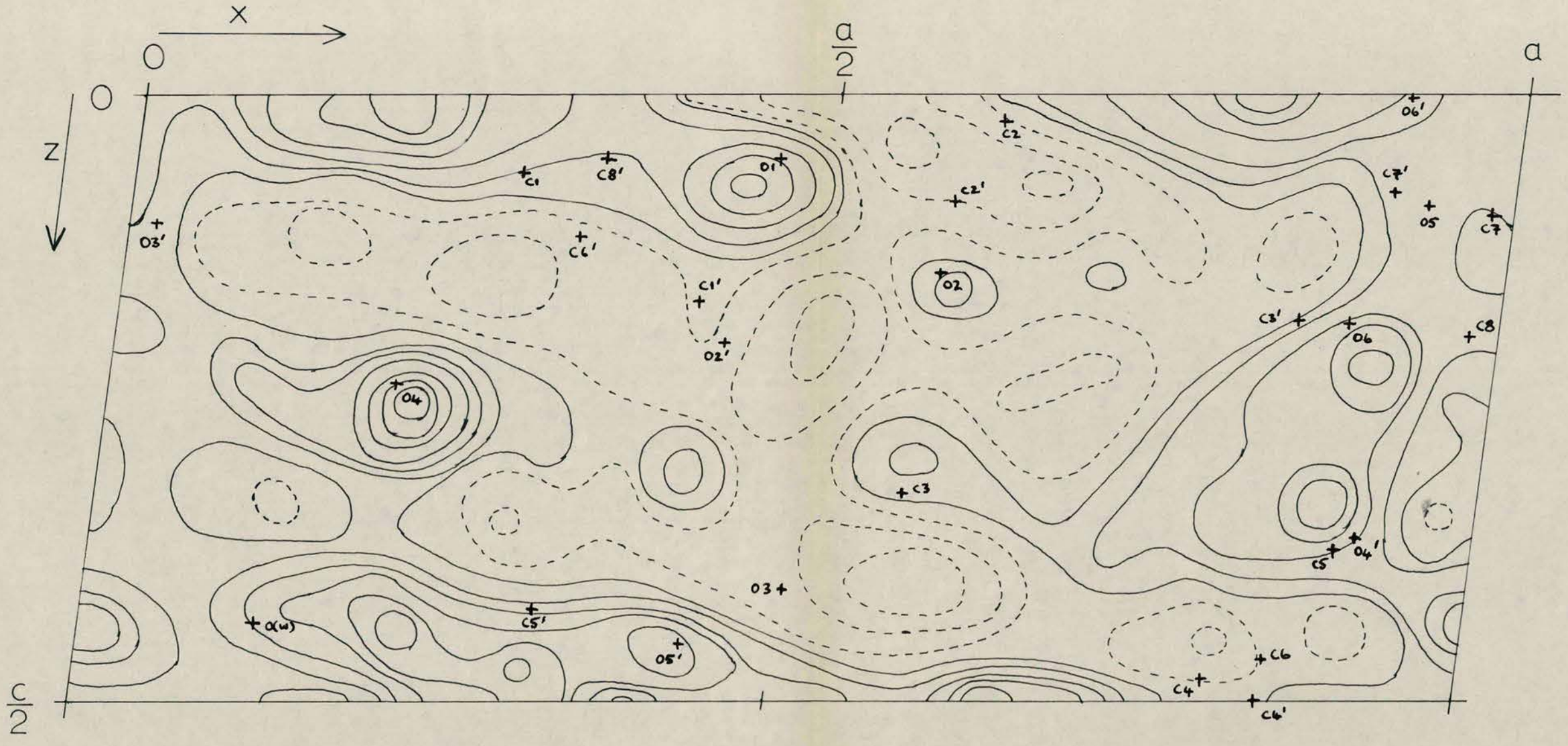


Fig (21)

Projection Patterson on to (010)

Moderate Sharpening

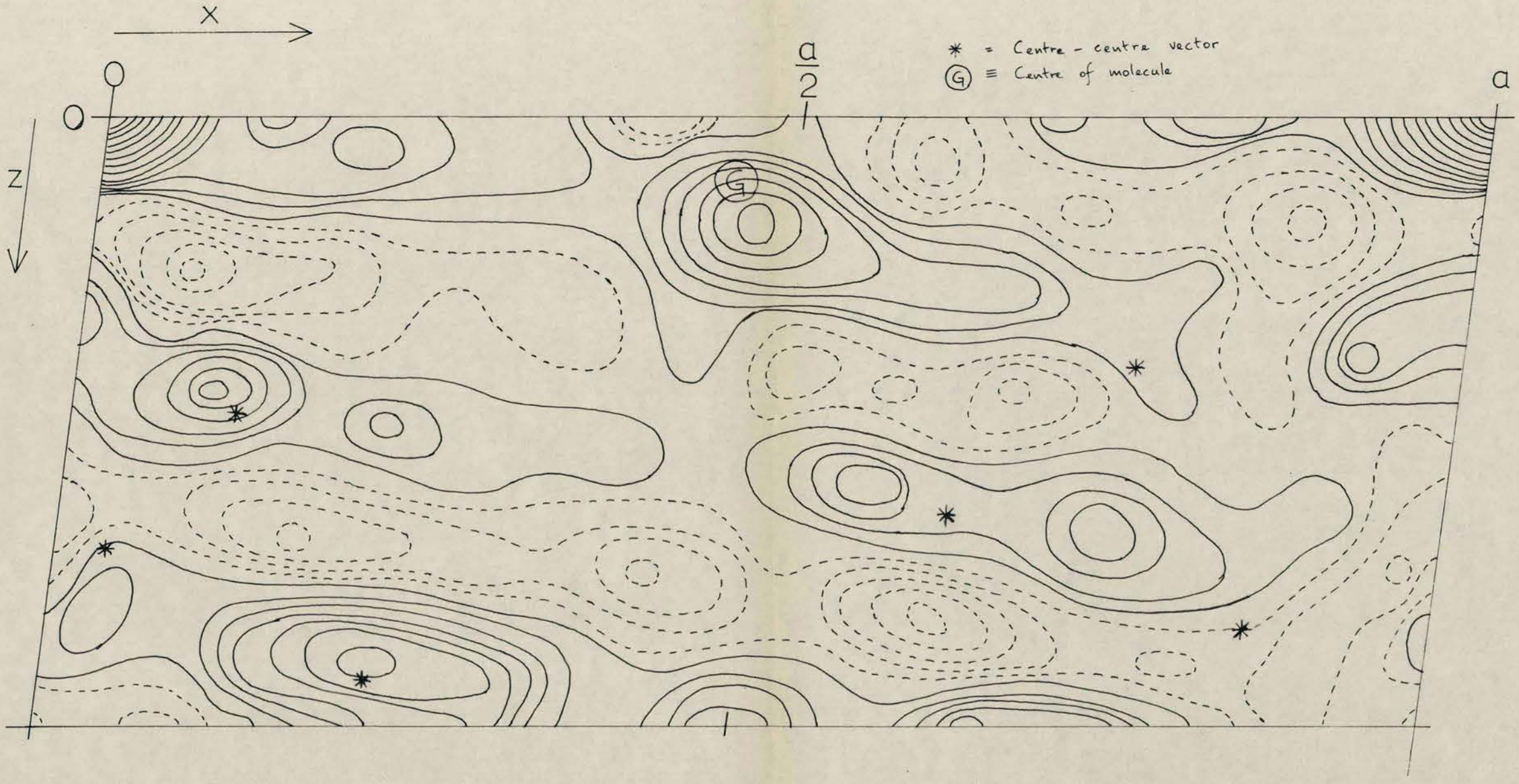


Fig (22)

Projection Patterson on to (010)

"Point Atom at Rest" Sharpening

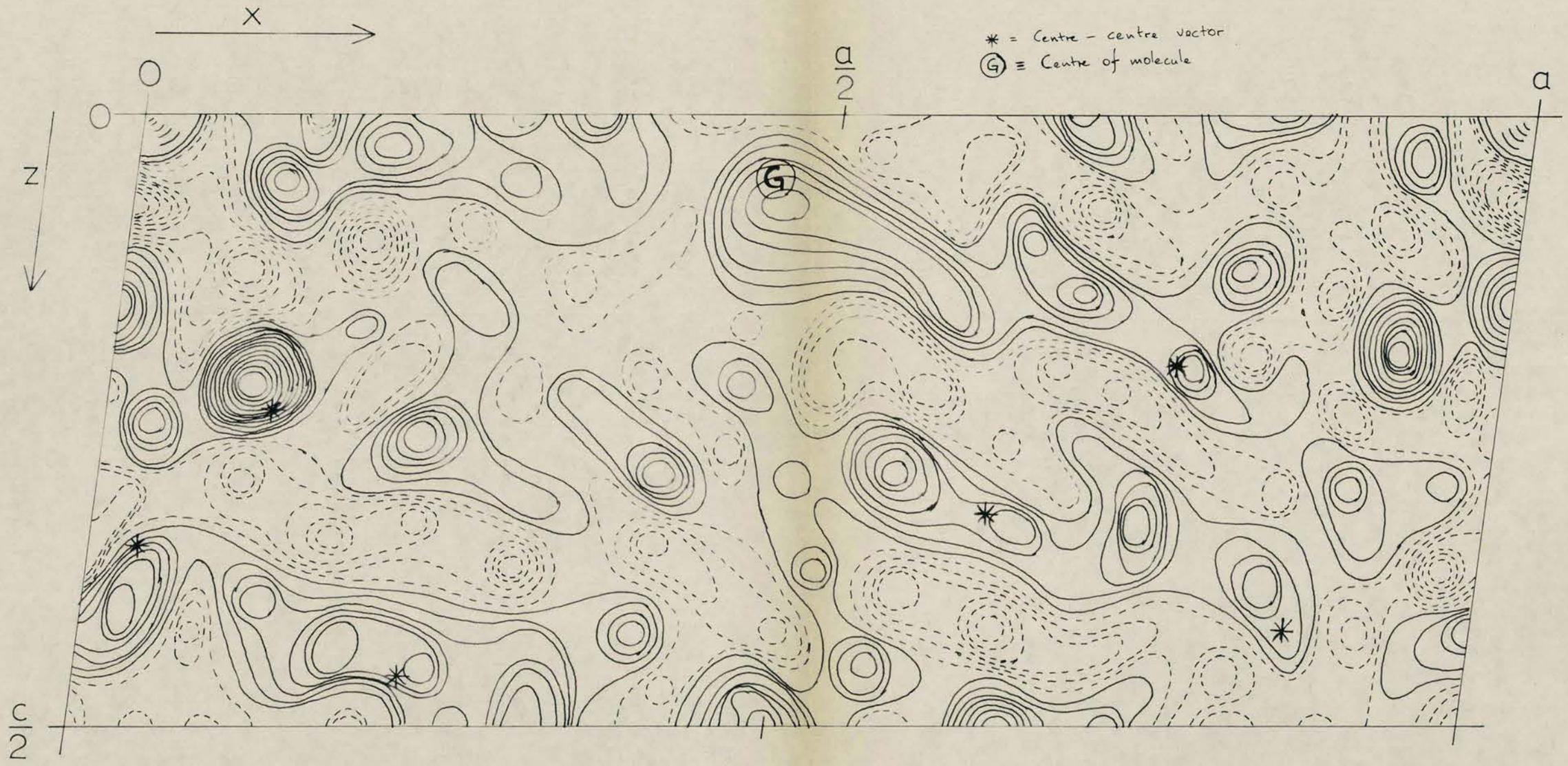


Fig (23)

Patterson map projected on to (010), the only centrosymmetric projection in space group $P2_1$, each double ring should give rise to a characteristic line of three strong peaks. In addition to these principal peaks, several satellite peaks should also be present, as was the case for α,α-trehalose.

The orientations of the two double rings were known to be related by a mirror plane lying almost parallel to the (010) plane. It was therefore expected that centre-centre peaks would be present due to the fact that the point half way between two crystallographically unrelated rings would be surrounded by a considerable number of atoms approximately related by centrosymmetry. These peaks must also lie in lines parallel to the 5 Å vector across the double ring. Many such peaks were known to be present. Some of these peaks relate the two double rings of one molecule, so it was correctly predicted that a long line of peaks, 2.5 Å apart, should extend from the origin of the projection Patterson map in the known direction of the molecule. It was unfortunate that some of the true centre-centre vectors also fell on this line. In consequence the maps contained peaks which were extended roughly along the x direction, so that considerable ambiguities existed as to the interpretation of these peaks. Although this difficulty was never resolved satisfactorily by Patterson methods, it was encouraging to obtain confirmation that the general lie of the molecule was as expected.

The next stage was to search for a set of centre-centre peaks for both double rings. The two sets of three peaks had to be almost collinear, and when a possible set of peaks had been selected it was possible to seek other large peaks due to the vectors between unrelated rings as a

check. The restriction that the centre of the molecule must lie near the point ($x=\frac{1}{4}, z=\frac{1}{2}$), discussed above (p.91), was now very useful in limiting the selection of sets of peaks. The four points ($\frac{1}{4},\frac{1}{2}$), ($\frac{1}{4},0$), ($\frac{3}{4},\frac{1}{2}$) and ($\frac{3}{4},0$) were equivalent, so one of them was chosen at random. The list of final atomic parameters presented later (Tables 26 and 28, p.114 and p.116) located the centre of the molecule at roughly ($\frac{1}{4},0$).

A peak was expected to appear in the (010) projection Patterson maps to correspond to the approximate centre-centre vector for the whole molecule and its symmetry-related molecule. This peak was expected to be diffuse but high. There was only one peak in both maps which fitted this description and lay close to the expected position of ($\frac{1}{2},0$). It was centred on the point (.475, .088) in the modestly sharpened map and (.462, .075) in the sharp map. It was calculated, from the final refined parameters, that the peak should have been centred on the point (.452, .056). The very sharp map thus yielded the better value, corresponding to an error of 0.1 Å, compared to 0.2 Å for the less sharp map, in the position of the molecule in the unit cell.

It was, however, considerably more difficult to determine the position of the double rings. Although they obviously lay on either side of the central position in approximately a straight line, the exact displacement of one with respect to the other was unknown. The correct positions of the true centre-centre vectors concerning each double ring are marked on the two maps shown (figs 22 and 23). It can be seen that the fit of these vectors is rather poor, particularly for the less sharp map. The exact location of the first half of the molecule was not found by Patterson methods, although several possible positions were tried. Amongst the

various possible positions of the second half of the molecule which were tried was included the correct one.

Two further ambiguities arose, for it was not known which half of the molecule was in which orientation, nor was it known which way the twenty atoms of the two double rings should be labelled, for there were two possibilities. These two difficulties could be overcome either by omitting the substituents to the rings and making the two ring orientations exact mirror images, or else by calculating large numbers of alternative Fourier syntheses. After many failures, the final position reached was that the trial structure had the double rings in the correct orientations, with the atoms labelled correctly, but displaced from the correct positions by as much as 0.5 Å. Refinement of this structure terminated with the residual, R = 40%. The agreement of the low angle structure factors was considerably better than this, suggesting that some small shift of the whole molecule, or half of it, might be the only large error.

A program was now written, in Atlas Autocode for the KDF9 computer, which produced a residual map, using only about half of the structure factors to save computing time. The higher angle structure factors were those omitted. The calculation allowed some atoms to remain stationary while the remainder were moved simultaneously over a grid of points. Small shifts of both halves of the molecule were indicated, but it appeared that the trial structure was in a substantial "false minimum". The residual was thus reduced to rather less than 40%.

Use was now made of the minimum residual method of refinement (A. K. Bhuiya and E. Stanley, 1963). All of the (h0ℓ) structure factors

were calculated. The contribution of the first atom in the list was now subtracted from all the structure factors. Its contribution was computed at each point on a 5 x 5 grid of points, with specified equal intervals. Structure factors were thus obtained, and a residual was calculated, for all the grid points. The atom was now moved to the grid point with the lowest residual, or, if the atom had moved to the edge of the grid, one interval further. New structure factors were then stored and the refinement process was repeated with the next atom in the list. The residual was thus reduced to R = 35%, but some of the bond lengths became unacceptably long at over 1.8 Å. It was therefore felt that although the trial structure was basically correct, it was not close enough to the solution for a successful refinement to commence.

(c) Three-dimensional Methods.

It was realised that the most probable error in the co-ordinates obtained above was a small overall displacement, although the magnitude of this shift was greater than that imagined. The most useful structure factors were likely to be those at intermediate values of $\sin\theta$. The low angle reflections are generally insensitive to small errors in atomic parameters, whereas the high angle reflections are too sensitive. The expected error might have had a drastic effect on the phase angles of high angle reflections. Accordingly, a three-dimensional electron density synthesis was computed using just under half of the observed data, eliminating the high angle reflections. The heights up the y axis were deduced with the aid of a model of the molecule. The peaks in the map produced were quite spherically symmetrical and there was no evidence of a general shift of many atoms.

If the accurate geometry of one molecule were known, then this information could be fitted into the approximate solution, either by model building or by further examination of the (010) projection Patterson maps, and a complete solution could be obtained. A three-dimensional minimum function was computed, using the atoms of one double ring as the starting positions. The map obtained was of hopelessly poor resolution, so a second superposition was carried out, including the ring substituent atoms in the starting set. This map was also of very poor resolution, so the geometry of the molecule was not established.

By pretending that the space group was triclinic rather than monoclinic a sum function was readily computed by Fourier methods. It was necessary to use reflections covering half, and not a quarter, of the reciprocal sphere. Since this included a very large number of reflections the smallest intensities were omitted from the list, since their contributions would have been negligible. The double ring and its substituents provided the input atomic positions. The sum function map produced in this way was no more informative than the minimum function had been.

4. DIRECT METHODS OF PHASE DETERMINATION

(a) The Application of the Σ_2 Relationship.

The observed intensities were converted into normalised structure factors, although due to the fact that the scale factor deduced from the Wilson plot was erroneous, the resultant list of E_h values was on average about 6% too high. The list contained 268 values ≥ 1.50. Of these, 101 were greater than 2.0, which was a clear indication that the values were too high. It was not planned that any use be made of the absolute $|E_h|$ values, so this mis-scaling was ignored. A second list was later prepared using the K-curve program written by Dr. Scott. The two lists agree quite well, the largest discrepancies being of about 7% when the effect of the scaling error is discounted. The lists are tabulated later in this thesis (Appendix V).

A program was written, in Atlas Autocode for the KDF9 computer, to carry out a Σ_2 listing for all the 268 reflections with $E'_h \geq 1.50$ (where E'_h is defined as the modulus of the mis-scaled normalised structure factor). This program was later modified to carry out tangent formula refinements one cycle at a time. The full listing consisted of rather an unwieldy amount of paper, so a second listing was abstracted from it, restricted to those $E'_h > 2.0$. Since three of the E'_h values greater than 2.0 were not accessible at this level, the shorter listing contained 249 relations involving 98 different reflections.

The desiderata in starting a phase determination have been discussed above (p.47). The method outlined here was based on the earlier work

described above. For space group $P2_1$ it was found to be necessary to resist the temptation to include too many reflections from the centrosymmetric zone in the starting set of phases. A list of all the reflections which were thought to be possible members of the starting set is shown below (Table 22).

****

TABLE 22

Possible Starting Reflections.

h	k	ℓ	E'_h	NR	φ	h	k	ℓ	E'_h	NR	φ
-12	0	6	3.40	9		-5	3	6	2.52	15	
-10	0	1	2.37	7		-4	3	1	2.11	18	
-6	0	8	3.36	11	a	-2	4	2	2.27	15	
-1	0	5	4.97	18	0	1	2	0	2.04	25	
4	0	2	2.48	10		3	1	7	2.42	12	c
4	0	7	2.74	8	0	4	1	7	3.71	16	0
6	0	2	2.37	7		5	1	2	2.13	15	
						6	1	1	2.12	16	
						6	5	0	2.99	16	b

NR is the number of relations in which the reflection takes part. φ shows the reflections used in the starting set and their assigned phases in radians.

Two reflections were needed to fix the origin in the centrosymmetric projection, one of which had to have indices (odd,odd) whereas the other could have (even,odd) or (odd,even). The best choices were clearly (-1,0,5) and (4,0,7), which were both given plus signs, i.e. phase angle zero. The two best reflections from the non-centrosymmetric list were (4,1,7), which was given phase angle zero in order to fix the origin up the y axis, and (6,5,0), which was restricted to the range $0 \leqslant \varphi \leqslant \pi$ radians in order to specify the enantiomorph.

It was decided to use two further starting phases, one reflection each from the centrosymmetric and non-centrosymmetric lists. The choice of these two extra starting reflections was the first difficult decision, for different reflections or a different number of further reflections could equally well have been used. Since there were only a limited number of reflections to choose from, and since a preliminary examination of each choice required very little time compared to the later stages of the phase determination procedure, each possibility was scrutinised in turn. It is the opinion of the candidate that this was a very worthwhile operation.

Using the four starting reflections already established, each of the remaining centrosymmetric reflections was examined. With the shorter $\sum_2$ listing, it was found that the selection of (-6,0,8) would lead to most new phases being determined in one cycle of extension of the set. The more difficult decision was the choice of a third non-centrosymmetric reflection, for it was necessary to obtain a good spread of k values early in the phase determination process, as well as establishing as many new phases as possible. (3,1,7) fitted these conditions best,

although it was necessary to work through more than one cycle of phase extension in order to ensure that the phases determined did cover the range of k values adequately.

Successive cycles of application of the Σ_2 relationship soon led to the determination of the phases of 83 of the reflections for which $E'_h \geqslant 2$. This part of the calculation was very simple and was easily performed in one day. As there was a considerable excess of relations over unknown phases, there were many checks that the progress was satisfactory. There were also strong indications that $c = 0$ and that $b = \frac{\pi}{2}$; these values were accepted. The reflections used were not restricted to one quarter of the reciprocal sphere, but on changing from one quarter to another, the following changes of phase occurred:

	$(hk\ell)$	$(\bar{h}\bar{k}\bar{\ell})$	$(h\bar{k}\ell)$	$(\bar{h}k\bar{\ell})$
k even	α	$-\alpha$	$-\alpha$	α
k odd	α	$-\alpha$	$\pi-\alpha$	$\pi+\alpha$

It would obviously have been easy to use the tangent formula to extend and refine these 83 phases, but the candidate was handicapped by the fact that he was in Nigeria at the time, so that only the two Σ_2 listings were available to him. The Σ_2 relationship was therefore used to extend the phase determination downwards to those reflections for which $1.5 \leqslant E'_h < 2.0$. 129 further phases were thus obtained. As the new values were usually unweighted averages from several contributing relations the new values were not restricted to $0, \pi, \frac{\pi}{2}$ or $\frac{3\pi}{2}$ radians, unlike the initial 83 phases. Weak indications that $a = \pi$ were accepted. If the work done subsequently had been unsuccessful, then the alternative

substitution a = 0 would have been made and a fresh start would have been made at this point.

A few phases were calculated by three different methods, (i) an unweighted Σ_2 relationship, (ii) a form of the Σ_2 relationship in which each contributing relation was weighted according to the product $E'_h.E'_k.E'_{h-k}$ and (iii) a tangent formula calculation. The values obtained were closely similar, lying within about 0.1 radian. It therefore seemed pointless to expend a lot of effort to obtain weighted averages and so the simplest method was used again. Since there were generally about 15 contributors to each average, it would only be in a case where the individual contributors were widely spread that a significant change would occur on changing the method of calculation. Such a phase would be known to be inaccurate in any case.

All the 212 phases so far determined were now used in a refinement and extension process. 36 new phases were established, and two of the old list, (-4,4,6) and (-1,4,7), were rejected as their values were very uncertain. The phases of 246 reflections were thus determined. A second refinement process was now commenced. It was considerably more time consuming because now almost all the possible relations were contributing to each phase. The changes in phase between this cycle and the previous one were very small, averaging less than 0.1 radian for the non-centrosymmetric reflections. When about a quarter of the phases had been refined it was decided to abandon the process. No new phases had been added to the list, but one, (-13,4,2), was rejected, so that the final list was of 245 phases.

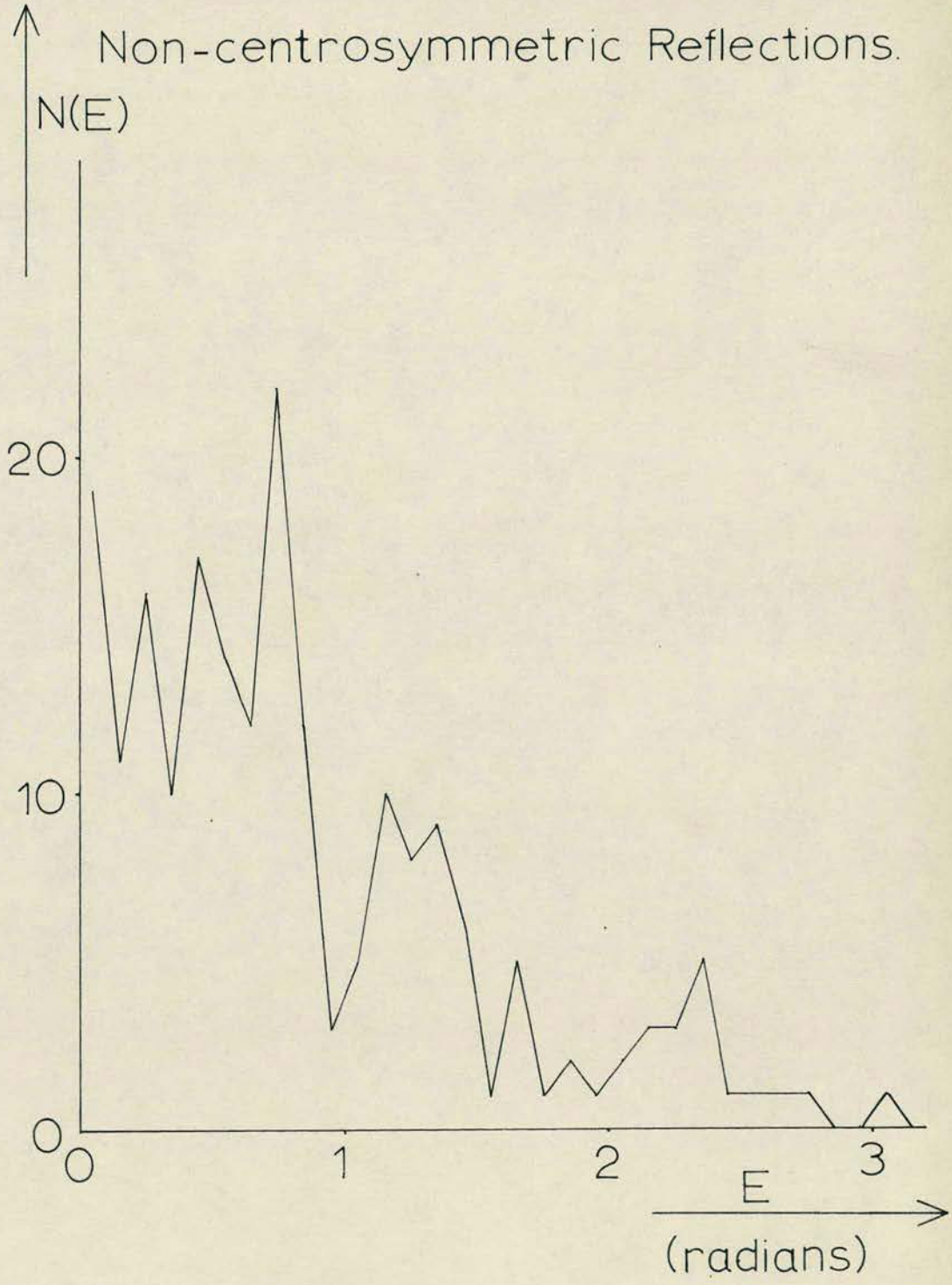
A list of the phases obtained compared to the corresponding values calculated from the final refined parameters is presented (Appendix V). Of the 44 phases of centrosymmetric reflections, 30 were correctly determined and 14 were wrong. The distribution of errors in the calculated phases of non-centrosymmetric reflections compared to the corresponding values for the final refined structure are shown in a graph (fig 24). One reflection, (10,0,7), was included in the phase determination but omitted from the refinement, since it was too near the edge of the film to be measured accurately.

This was a much less accurate phase determination than the two described for α,α-trehalose. This was no doubt partly due to the fact that the E_h' data used were inferior. The errors in the data for diethylidene trehalose were larger and included extinction effects, which caused some very useful reflections to be weighted down below their true level. More important, however, was the fact that space group $P2_1$ is less suited to the direct method approach than $P2_12_12_1$, for the latter contains much more useful centrosymmetric reflections.

(b) The Solution of the Structure.

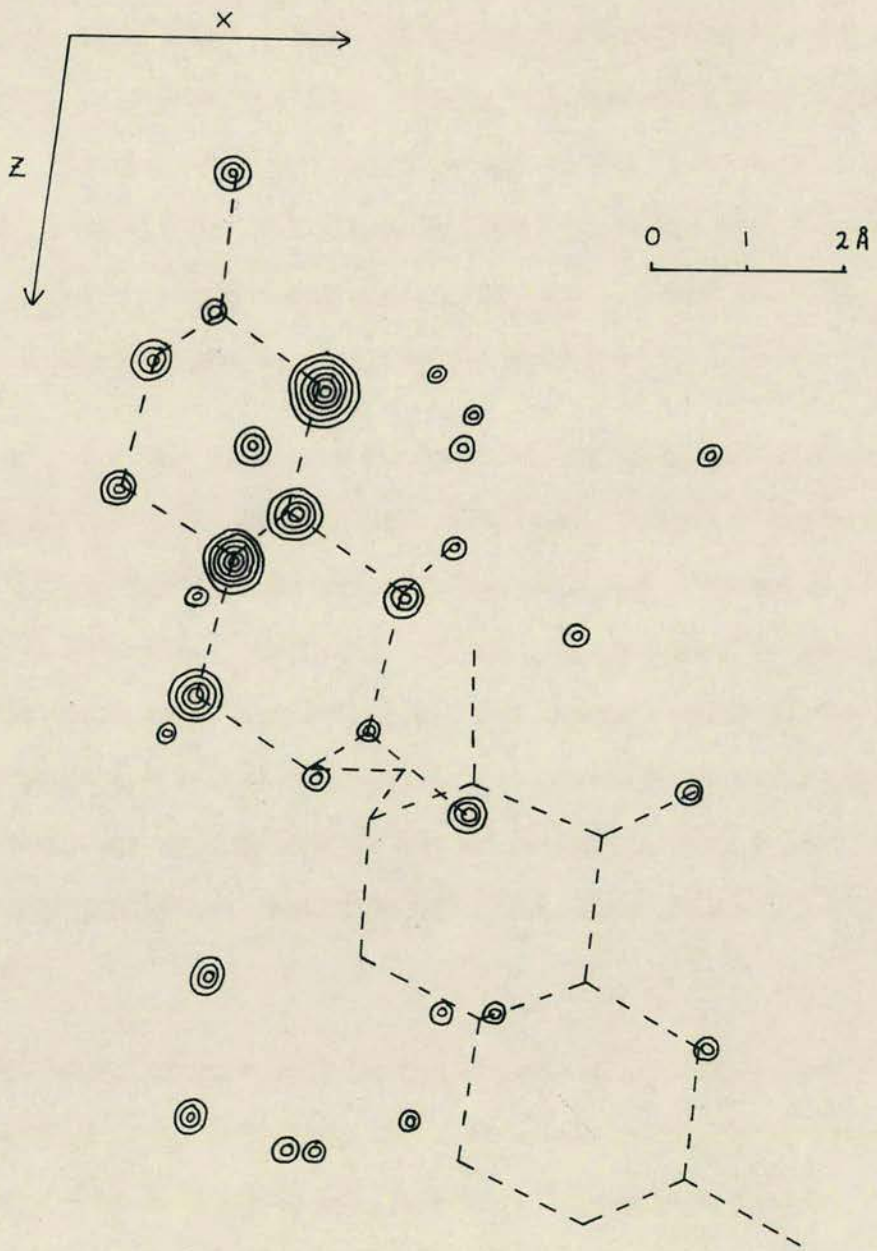
During the candidate's absence overseas, the language used for computing was changed to Fortran IV. Although it had been planned to refine the 245 phases using the tangent formula program written previously, it was decided to use the successful Multan system instead. Two attempts were made to obtain a solution of the structure by this method, but although both times the figure of merit was greater than 1.1, in neither case was the resultant E-map interpretable.

Graph of Distribution of Errors in Calculated Phases of Non-centrosymmetric Reflections.



(fig 24)

E-Map.



(fig 25)

It was now possible to refine the 245 phases using the FASTAN program, but an E-map was computed from them before this was tried and the refinement found to be unnecessary. This map (fig 25) clearly revealed half of the molecule. All the substituent atoms to this double ring were present, although O(1) did not appear in quite the expected position. Two atoms from the other half of the molecule also showed up in this map, but they were not close enough to the first double ring to be identified positively. All the intensity data could now be used to calculate structure factors and phases, followed by either an electron density synthesis or by a tangent formula refinement.

In calculating the structure factors all the 13 atoms located were assigned equal isotropic temperature factors B = 2.15 Å^2. The scaling was such that the sums of the observed and calculated structure factors were equal. The residual was R = 53.6%. An electron density synthesis was computed which contained 13 large peaks corresponding to the input atomic positions and numerous lesser peaks whose height was about one sixth as great. The second half of the molecule was now located, each of the new atomic positions coinciding with one of the smaller peaks in the Fourier map.

A second cycle of structure factor calculation and electron density synthesis was now computed using these 27 atoms as input positions. Again all the atoms were assigned equal isotropic temperature factors B = 2.15 Å^2. The residual fell to R = 38.0%, with significantly better agreement for the low angle reflections, clearly indicating that the structure was substantially correct. One extra peak was found in this map, apart from those due to the input atoms. It was interpreted as the oxygen atom, O(W),

of the water molecule. It was located so that the nearest atoms to it were three other oxygen atoms, O(2'), O(3') and O(6'), at suitable separations for hydrogen bonding.

The structure was thus solved by direct methods, but it should be noted that the interpretation of the E-map and of the electron density synthesis which followed it was greatly facilitated by the knowledge of the orientation and position of the molecule which was obtained by Patterson methods. In retrospect it seems that had work been continued with the earlier trial structure then the solution would eventually have been obtained. It might be suggested that the effect of using a poor set of intensity data was more prejudicial to the chance of success by direct methods than by Patterson methods, as is evidenced by the failure of the two attempts to employ the Multan system. On the other hand, it does appear that carbohydrate structures are well suited to direct methods of solution, especially since a trisaccharide structure has now been determined in this way (H. M. Berman, 1970).

5. THE REFINEMENT OF THE STRUCTURE

The atomic scattering factors used in the refinement were as before (Oxygen: A. J. Freeman, 1959; Carbon: J. Berghuis, et al., 1955; Hydrogen: R. McWeeny, 1951). The enantiomorph had been specified at random and the choice made was the wrong one. The entire refinement was carried out with the mirror image of the correct structure. The parameters quoted (Tables 26, 27 and 28) therefore apply to the L-sugar, but the diagram (fig 26) shows the correct D-sugar, obtained by a mirror operation about the plane (010).

The positions of the 28 carbon and oxygen atoms in the asymmetric unit of the structure were now subjected to two cycles of refinement by electron density synthesis. The bond lengths and angles were so modified by this refinement that they became closer to the expected values. The residual fell to R = 22.9%. The low angle structure factors showed considerably better agreement than this whereas those at high angles were worse.

The refinement was continued by the method of least squares. The program which was used to perform the calculations used the block diagonal simplification. The three positional parameters and an isotropic thermal vibration parameter for each atom were varied, each atom being treated separately. This meant that although there was no restraint to fix the origin up the y axis, each atom was moved up or down it with respect to the other twenty-seven, so that the origin was not really free to float. The weighting scheme employed gave each structure factor a weight equal to the reciprocal of its estimated standard deviation (Table 19).

Two cycles of refinement reduced the residual to less than 16%, excluding the non-systematically absent reflections. The thermal parameters assumed reasonable values. For the atoms in the glucose rings $1.7 < B < 2.1$ Å^2, whereas those in the rings closed by the ethylidene groups and the other substituents to the glucose rings had somewhat higher values. The carbon atoms of the methyl groups had $B = 3.0$ and 3.4 Å^2 and for the oxygen atom of the water molecule $B = 4.7$ Å^2. The shifts in the thermal and positional parameters of the atoms had become quite small, so it was decided to try to locate the hydrogen atoms.

Structure factors and a difference Fourier synthesis were computed. The residual, which now included the non-systematically absent reflections, rose to $R = 16.9\%$. The best agreement was in the middle of the range of $\sin\theta$ values. This was because the contribution of the hydrogen atoms to the low angle structure factors was now significant. It was possible to locate 22 of the 28 hydrogen atoms in the asymmetric unit from this map. No attempt was ever made to refine these positions since the observed intensity data were not sufficiently accurate.

The only hydrogen atoms which were not located were the six in the two methyl groups. They were either free to rotate about the C(7) - C(8) bond, or, more probably, to oscillate over quite a large arc. The carbon atoms of the methyl groups were subject to much greater thermal vibrations than the other atoms of the molecule, and it appeared that their vibrations were distinctly anisotropic. It was therefore thought that it would not be possible to locate these atoms with the available data. It should be pointed out that the thermal vibration parameters of atoms

C(8) and C(8') are not valid. They are compensating for the missing hydrogen atoms as well as representing the thermal vibrations of the carbon atoms.

One further cycle of refinement by the method of least squares was carried out with isotropic thermal parameters. In this and subsequent calculations the hydrogen atoms were assigned equal isotropic thermal parameters B = 2.5 Å^2. Four parameters for each of the 28 oxygen and carbon atoms and the overall scale factor were refined. The residual fell to 13.4%, the final value for the isotropic refinement. The shifts in the positional parameters were now small, the two biggest being of three-quarters of an estimated standard deviation. It transpired that some of the low order reflections suffered badly from secondary extinction, the final evidence for which is given below (Table 23).

Anisotropic thermal vibration parameters were introduced, so that the parameters refined consisted of one overall scale factor together with three positional and six thermal parameters for each of the 28 oxygen and carbon atoms, making 253 in all. Some quite large positional shifts were indicated, although several parameters wobbled to and fro in the five cycles of refinement which were performed. The magnitude of the shifts fell as the refinement proceeded, as did $\Sigma\omega\Delta^2$, the quantity minimised. The residual, however, only fell slightly, as can be seen in the summary of the progress of the refinement (Table 24). Although structure factors were calculated for the reflections which were badly affected by secondary extinction, they were not allowed to contribute to the shifts applied to the parameters.

These calculations revealed the disturbing fact that the intensity data were badly mis-scaled. The structure factor list from the eighth cycle of the least squares refinement was used to calculate new scale factors to relate together the various layers of crude intensity data. The rescaling process was thus analogous to the original scaling except that it was performed backwards. When the amended scale factors had been calculated it was a simple matter to produce a complete set of rescaled data. It is probable that the mis-scaling was due to absorption errors. These would arise because the crystal specimens employed did not have exactly circular cross-sections.

The weighting scheme for the refinement was amended to the more proper form in which the weight given to a structure factor is proportional to the reciprocal of the square of its estimated standard deviation. This alteration changed the value of $\sum \omega \Delta^2$ considerably, but otherwise had very little effect. Two further cycles of refinement of the same 253 parameters served to converge the refinement. Although the residual fell considerably in the last cycle, the value of $\sum \omega \Delta^2$ fell only slightly (Table 24). The final indicated shifts were small, the largest shifts in the positional parameters being about one third of an estimated standard deviation.

The final stage of the refinement was to calculate a difference Fourier synthesis. Structure factors were calculated for all the intensity data, for which the residual was R = 12.2%. The analysis of agreement of these structure factors is reproduced below (Table 25). The relatively poor agreement of the lowest angle structure factors was due, in part, to the extinction errors. The most prominent features in the difference

Fourier synthesis were diffuse peaks close to atoms C(8) and C(8'). These were attributed to the missing hydrogen atoms and, possibly, to the inadequate thermal vibration parameters of the two carbon atoms. It was not possible to locate the hydrogen atoms satisfactorily from the map, so it was felt that any attempt to include them in further calculations would not bring about a significant extension of the refinement.

Lists of the final atomic parameters, i.e. those used to calculate the final difference Fourier synthesis, are given below (Tables 26, 27 and 28).

TABLE 23

The Evidence of Secondary Extinction.

h	k	ℓ	$\sin^2\theta$	$\lvert F_{obs}\rvert$	$\lvert F_{calc}\rvert$	$\frac{\lvert F_{calc}\rvert}{\lvert F_{obs}\rvert}$
-2	0	1	0.02	664	963	1.450
-2	1	1	0.03	587	889	1.514
-2	1	2	0.05	462	436	0.944
-2	1	3	0.07	469	420	0.896
-1	0	3	0.05	626	505	0.807
-1	2	1	0.04	573	706	1.232
0	0	1	0.01	464	489	1.054
0	0	2	0.02	518	434	0.838
0	1	1	0.01	633	839	1.325
0	2	0	0.03	495	541	1.093
1	2	0	0.04	725	1003	1.383
2	0	1	0.03	582	650	1.116
2	1	0	0.03	491	557	1.134
2	2	0	0.05	518	573	1.106
4	0	0	0.08	582	619	1.064

TABLE 24

A Summary of the Refinement by the Method of Least Squares.

Cycle	Atoms	Thermal Parameters	R_{input}	$\sum \omega \Delta^2_{input}$
1	C,O	C,O isotropic	20.46%	61743
2	C,O	"	16.04	42942
3	C,O and H	"	14.41	33802
4	"	C,O anisotropic	13.82	31141
5	"	"	13.38	26950
6	"	"	11.97	24486
7	"	"	12.24	19892
8	"	"	11.42	16959
*** Data Re-scaled and Re-weighted ***				
9	"	"	10.74	46079
10	"	"	10.22	43552

TABLE 25

Analysis of Agreement for the Final Structure Factors.

(i) Against $\sin^2\theta$:

$\sin^2\theta$	$\Sigma\|F_{obs}\|$	$\Sigma\|F_{calc}\|$	$\Sigma\|F_o-F_c\|$	R
0.0 - 0.1	22668	23442	3455	0.15
0.1 - 0.2	27893	27068	2780	0.10
0.2 - 0.3	22855	22054	2271	0.10
0.3 - 0.4	23245	23001	2090	0.09
0.4 - 0.5	22547	22844	2033	0.09
0.5 - 0.6	18884	19236	1931	0.10
0.6 - 0.7	14456	14851	2075	0.14
0.7 - 0.8	10425	10669	2017	0.19
0.8 - 0.9	9971	10099	2109	0.21
0.9 - 1.0	8222	7872	1323	0.16

(ii) Against $|F|$:

Fraction of $\overline{|F|}$	$\Sigma\|F_{obs}\|$	$\Sigma\|F_{calc}\|$	$\Sigma\|F_o-F_c\|$	R
0.00 - 0.25	1396	4219	3185	2.28
0.25 - 0.50	14114	13480	2450	0.17
0.50 - 0.75	22575	21917	2883	0.13
0.75 - 1.00	22706	22157	2279	0.10
1.00 - 1.25	16217	16100	1415	0.09
1.25 - 1.50	14949	14725	1347	0.09
1.50 - 1.75	12278	12154	964	0.08
1.75 - 2.00	9088	8566	858	0.09
2.00 - 2.25	10338	10152	788	0.08
$\geqslant$ 2.25	57507	57719	5968	0.10

(iii) Against the Miller Indices:

h	R	k	R	ℓ	R
0	0.13	0	0.18	0	0.10
1	0.13	1	0.13	1	0.11
2	0.13	2	0.10	2	0.10
3	0.12	3	0.10	3	0.14
4	0.10	4	0.10	4	0.13
5	0.11	5	0.12	5	0.11
6	0.09	6	0.10	6	0.12
7	0.12	7	0.12	7	0.12
8	0.13	8	0.14	8	0.13
9	0.16	9	0.19	9	0.16
$\geqslant$ 10	0.15	$\geqslant$ 10	0.20	$\geqslant$ 10	0.21

TABLE 26

Carbon and Oxygen Atoms:

Final Fractional Co-ordinates and Estimated Standard Deviations.

Atom	x	E.S.D.	y	E.S.D.	z	E.S.D.
C(1)	0.14067	0.00065	0.23890	0.00127	0.03167	0.00077
C(2)	0.18998	0.00070	0.39123	0.00117	0.98766	0.00078
C(3)	0.21078	0.00072	0.38475	0.00111	0.83618	0.00082
C(4)	0.09216	0.00067	0.33243	0.00117	0.75873	0.00077
C(5)	0.04921	0.00065	0.18107	0.00118	0.81346	0.00080
C(6)	0.07078	0.00071	0.63480	0.00133	0.26675	0.00086
C(7)	0.00920	0.00079	0.76461	0.00128	0.45254	0.00087
C(8)	0.01190	0.00107	0.23451	0.00145	0.40115	0.00090
O(1)	0.23097	0.00046	0.12266	0.00076	0.02660	0.00053
O(2)	0.29563	0.00055	0.44090	0.00090	0.07202	0.00058
O(3)	0.24755	0.00050	0.53401	0.00082	0.79598	0.00059
O(4)	0.10549	0.00049	0.30516	0.00083	0.61972	0.00052
O(5)	0.03203	0.00045	0.19584	0.00077	0.95346	0.00051
O(6)	0.05233	0.00053	0.62484	0.00091	0.40536	0.00058
C(1')	0.20856	0.00070	0.97696	0.00114	0.08492	0.00083
C(2')	0.29659	0.00068	0.85636	0.00118	0.04330	0.00074
C(3')	0.42646	0.00070	0.90455	0.00106	0.09587	0.00080
C(4')	0.42833	0.00068	0.91278	0.00113	0.25018	0.00079
C(5')	0.33718	0.00071	0.02756	0.00112	0.28823	0.00080
C(6')	0.33767	0.00071	0.02659	0.00139	0.44085	0.00085
C(7')	0.45641	0.00075	0.45058	0.00131	0.53944	0.00075
C(8')	0.33222	0.00087	0.50141	0.00179	0.47293	0.00091
O(2')	0.28021	0.00054	0.84714	0.00087	0.89773	0.00054
O(3')	0.48943	0.00053	0.30101	0.00094	0.94698	0.00056
O(4')	0.45802	0.00049	0.46031	0.00086	0.68364	0.00052
O(5')	0.21807	0.00046	0.98602	0.00080	0.22750	0.00050
O(6')	0.45805	0.00051	0.05899	0.00089	0.50262	0.00057
O(W)	0.43670	0.00091	0.04717	0.00142	0.78579	0.00072

These co-ordinates refer to the wrong enantiomorph; for y read (1-y).

TABLE 27

Carbon and Oxygen Atoms:

Final Anisotropic Thermal Vibration Parameters.

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{31}	B_{12}
C(1)	0.00350	0.01319	0.00499	-0.00105	0.00162	0.00171
C(2)	0.00453	0.01056	0.00537	-0.00015	0.00325	-0.00005
C(3)	0.00487	0.00769	0.00622	-0.00068	0.00132	-0.00023
C(4)	0.00420	0.00898	0.00503	-0.00023	0.00278	-0.00031
C(5)	0.00352	0.00992	0.00584	0.00033	0.00324	0.00024
C(6)	0.00485	0.01232	0.00651	-0.00014	0.00288	0.00472
C(7)	0.00583	0.01097	0.00625	-0.00035	-0.00311	0.00397
C(8)	0.01249	0.01207	0.00529	-0.00470	-0.00021	-0.00316
O(1)	0.00463	0.00673	0.00563	0.00037	0.00145	-0.00183
O(2)	0.00657	0.01120	0.00593	-0.00401	0.00045	-0.00152
O(3)	0.00523	0.00759	0.00720	-0.00026	0.00142	-0.00276
O(4)	0.00490	0.01167	0.00399	-0.00010	0.00073	-0.00135
O(5)	0.00398	0.01038	0.00401	-0.00010	0.00306	0.00009
O(6)	0.00636	0.01188	0.00582	0.00240	-0.00028	0.00392
C(1')	0.00449	0.00823	0.00719	0.00157	0.00510	-0.00370
C(2')	0.00452	0.01047	0.00434	0.00072	0.00238	-0.00100
C(3')	0.00450	0.00652	0.00577	0.00038	0.00233	0.00157
C(4')	0.00414	0.00846	0.00554	0.00165	0.00180	-0.00020
C(5')	0.00532	0.00543	0.00646	0.00073	0.00364	0.00145
C(6')	0.00440	0.01495	0.00623	-0.00207	0.00212	0.00198
C(7')	0.00585	0.01247	0.00390	0.00078	0.00282	-0.00281
C(8')	0.00620	0.02770	0.00576	0.00821	-0.00308	-0.00150
O(2')	0.00631	0.01174	0.00405	-0.00154	0.00059	-0.00024
O(3')	0.00551	0.01601	0.00486	0.00210	0.00171	-0.00443
O(4')	0.00473	0.01260	0.00418	0.00208	0.00083	0.00086
O(5')	0.00391	0.01183	0.00422	0.00176	0.00206	0.00077
O(6')	0.00611	0.01233	0.00515	-0.00206	0.00185	0.00098
O(W)	0.01877	0.03238	0.00596	-0.00805	0.00986	-0.02755

TABLE 28

Approximate Fractional Co-ordinates of the Hydrogen Atoms.

Atom	Bonded to	x	y	z
H(1)	C(1)	0.125	0.250	0.138
H(2)	C(2)	0.125	0.467	0.010
H(3)	C(3)	0.260	0.307	0.820
H(4)	C(4)	0.043	0.423	0.768
H(5)	C(5)	0.100	0.083	0.780
H(6)	C(6)	0.038	0.733	0.275
H(7)	C(6)	0.093	0.523	0.250
H(8)	C(7)	0.025	0.383	0.545
H(9)	O(2)	0.350	0.393	0.030
H(10)	O(3)	0.318	0.517	0.775
H(11)	C(1')	0.120	0.907	0.050
H(12)	C(2')	0.288	0.733	0.050
H(13)	C(3')	0.430	0.025	0.090
H(14)	C(4')	0.415	0.800	0.245
H(15)	C(5')	0.340	0.150	0.288
H(16)	C(6')	0.330	0.917	0.450
H(17)	C(6')	0.285	0.117	0.460
H(18)	C(7')	0.465	0.317	0.525
H(19)	O(2')	0.275	0.733	0.885
H(20)	O(3')	0.470	0.207	0.905
H(21)	O(W)	0.375	0.983	0.813
H(22)	O(W)	0.440	0.067	0.693

6. DISCUSSION OF THE STRUCTURE

The final structure is shown projected on to the (010) plane (fig 26); the list of atomic co-ordinates (Table 26) has been operated on by a mirror plane coincident with the (010) plane, so that the correct enantiomorph has been reproduced. The molecules are held together partly by a network of hydrogen bonds and partly by van der Waal's forces.

The six hydrogen bonds (fig 27 and Table 29) make use of all the six hydroxyl groups which are available. The lengths of the hydrogen bonds lie in the usual range of 2.7 to 2.9 Å, although the average length is rather greater than was the case for α,α-trehalose dihydrate. The hydrogen bonding is therefore much weaker for diethylidene trehalose.

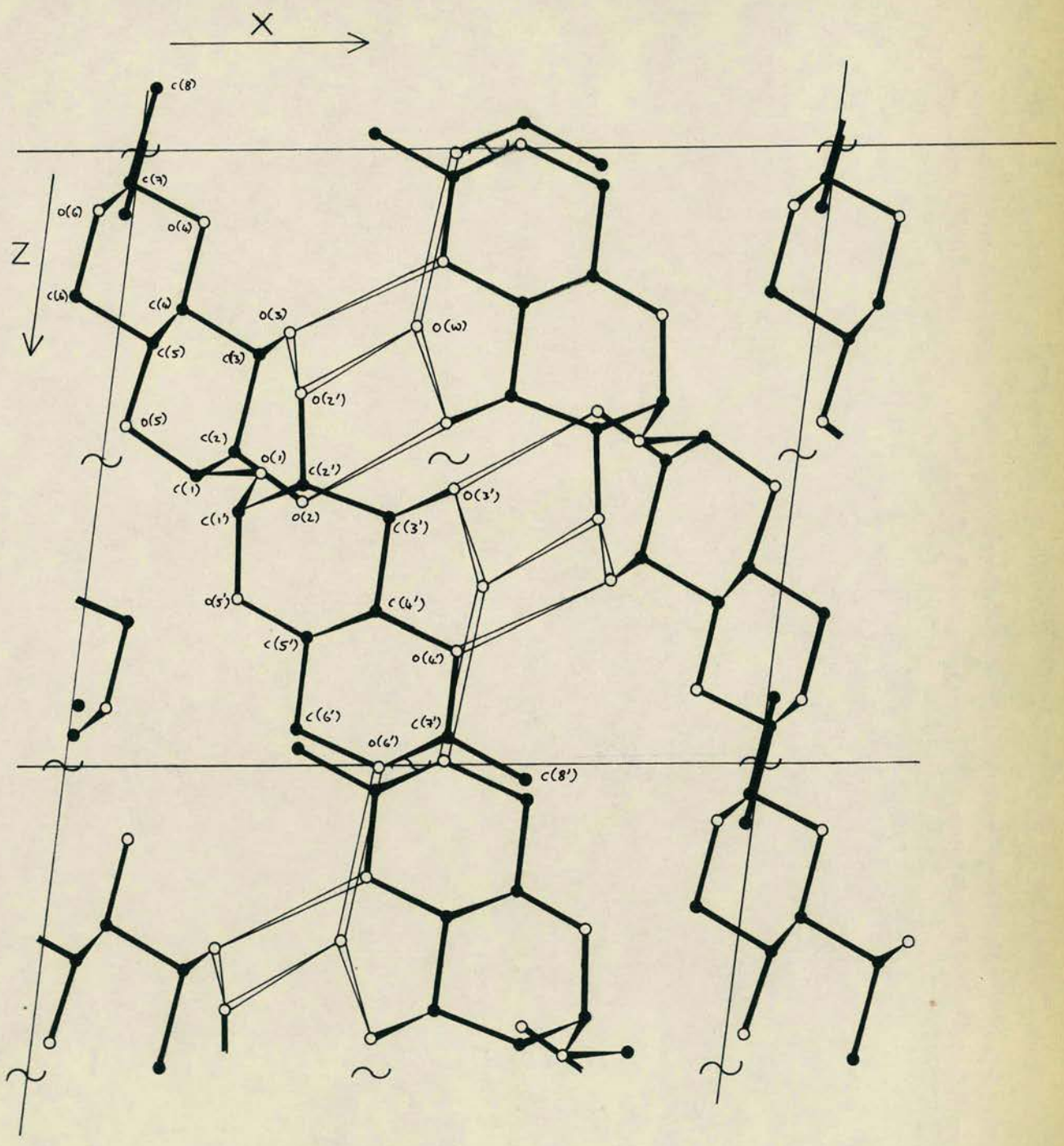
****

TABLE 29

The Hydrogen Bonds.

O —— H - - - - O			Length	E.S.D.
O(2)	H(9)	O(3')	2.908 Å	0.009 Å
O(3)	H(10)	O(4')	2.826	0.008
O(2')	H(19)	O(3)	2.837	0.010
O(3')	H(20)	O(W)	2.699	0.013
O(W)	H(21)	O(2')	2.781	0.012
O(W)	H(22)	O(6')	2.876	0.009

Diethylidene Trehalose.

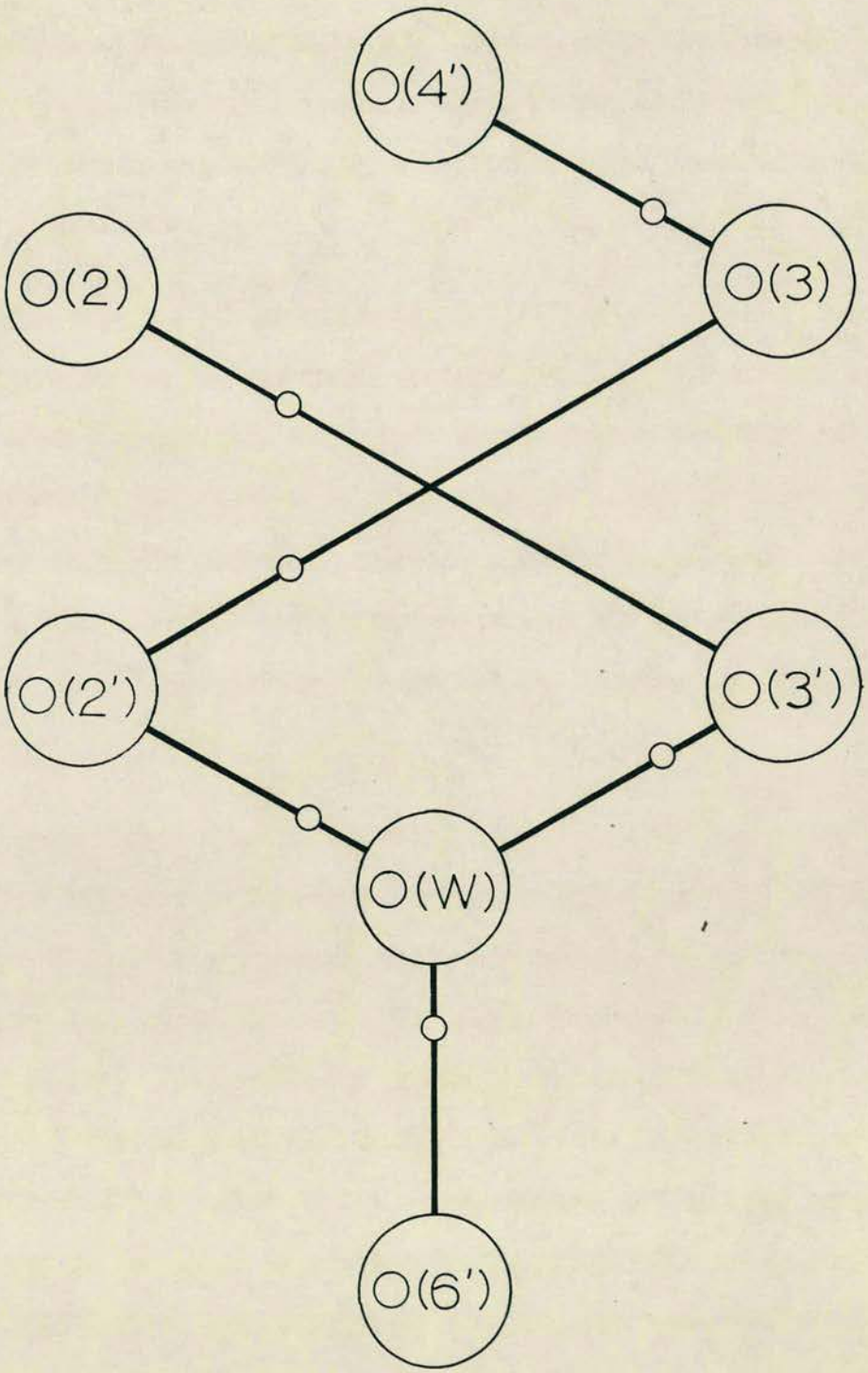


● = carbon o = oxygen

═══ = hydrogen bond 1 cm ≡ 1 Å

(fig 26)

The Hydrogen Bonds.



(fig 27)

As was found in the case of ∝,∝-trehalose dihydrate, there is no hydrogen bond in which O(1), the glucosidic oxygen atom, participates as an acceptor, nor is there an inter-residue bond of the type O(2) - H - - O(5'). Two of the oxygen atoms in the rings, O(4') and O(6'), function as acceptors in hydrogen bonds, which are 2.83 and 2.88 Å long respectively. Thus the three such bonds in the two structures which have been determined are all longer than average. The water molecule is trigonally co-ordinate.

There are some quite strong van der Waal's forces between molecules. The ethylidene groups on both sugar residues lie close to screw axes (fig 26), consequently there are rather short contact distances between each ethylidene group and the two other ethylidene groups related to it by the screw axis. The shortest separations of the carbon atoms are about 4.0 Å, but since the hydrogen atoms of the two methyl groups were not located, it is not possible to work out the shortest separations between atoms.

The conformation of the double rings is the expected one and the methyl groups attached to the double rings are in equatorial positions. This has the effect of minimising repulsions between the methyl groups and the lone pairs of electrons on the nearby oxygen atoms O(4) and O(6) or O(4') and O(6'). The bond angle at the glucosidic linkage was found to be 115.0° (three standard deviations = 1.9°) which is closely similar to the value of 115.7° obtained for ∝,∝-trehalose, and in good agreement with the results for other glycosides (Table 16, p.73). Newman projections down the C(1) - O(1) and C(1') - O(1) bonds are shown (fig 28).

The rotations about the C(1) - O(1) and C(1') - O(1) bonds are defined by the two dihedral angles:

$$C(1) - O(1) - C(1') - C(4') = 132.1^{\circ}$$
$$C(1') - O(1) - C(1) - C(4) = 127.4^{\circ}$$

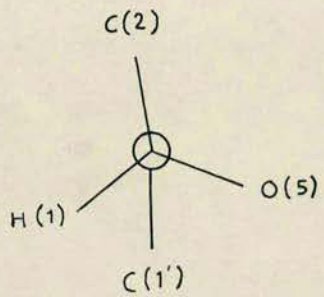
The corresponding angles for the ∝,∝-trehalose molecule were 120.7° and 134.7°, so the conformation at the glucosidic linkage is closely similar for both molecules.

The positional parameters of the hydrogen atoms were not refined, so estimated standard deviations were not calculated for these parameters. It was, therefore, impossible to calculate errors in the appropriate bond lengths and angles. The bond lengths and angles were themselves calculated in order to confirm that the hydrogen atoms were occupying reasonable positions. The rest of this discussion is concerned solely with the carbon and oxygen atoms.

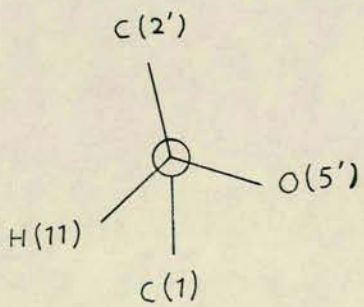
Lists of bond lengths and their estimated standard deviations (Table 30) and bond angles and their estimated standard deviations (Table 31) are shown for the carbon and oxygen atoms. The estimated standard deviations in both bond lengths and angles are on average about 2.5 times as large as the corresponding values for ∝,∝-trehalose dihydrate. The mean C - C and C - OH bond lengths for diethylidene trehalose were found to be 1.524 and 1.419 Å respectively, in good agreement with the results obtained in various accurate determinations of sugar structures (Table 17, p.75). The mean bond angle in the pyranose rings is 110.3°, in excellent agreement with previous results (Table 18, p.78).

Newman Projections.

(i) Down C(1) - O(1):



(ii) Down C(1') - O(1) :



(fig 28)

TABLE 30

Final Bond Lengths and their Estimated Standard Deviations.

Bond	Length	E.S.D.	Bond	Length	E.S.D.
C(1) - C(2)	1.489 Å	0.0137 Å	C(1') - C(2')	1.517 Å	0.0123 Å
C(2) - C(3)	1.565	0.0114	C(2') - C(3')	1.544	0.0111
C(3) - C(4)	1.520	0.0112	C(3') - C(4')	1.543	0.0113
C(4) - C(5)	1.495	0.0132	C(4') - C(5')	1.497	0.0121
C(5) - C(6)	1.530	0.0113	C(5') - C(6')	1.526	0.0118
C(7) - C(8)	1.535	0.0128	C(7') - C(8')	1.530	0.0133
C(2) - O(2)	1.429	0.0102	C(2') - O(2')	1.446	0.0093
C(3) - O(3)	1.401	0.0113	C(3') - O(3')	1.398	0.0107
C(1) - O(1)	1.419	0.0108	C(1') - O(1)	1.398	0.0112
C(1) - O(5)	1.411	0.0092	C(1') - O(5')	1.418	0.0098
C(5) - O(5)	1.444	0.0096	C(5') - O(5')	1.442	0.0096
C(4) - O(4)	1.437	0.0095	C(4') - O(4')	1.420	0.0096
C(7) - O(4)	1.437	0.0105	C(7') - O(4')	1.443	0.0092
C(6) - O(6)	1.432	0.0105	C(6') - O(6')	1.441	0.0100
C(7) - O(6)	1.382	0.0126	C(7') - O(6')	1.432	0.0115

TABLE 31

Final Bond Angles and their Estimated Standard Deviations.

	Angle	E.S.D.		Angle	E.S.D.
O(5) C(1) O(1)	112.13°	0.67°	O(5') C(1') O(1)	112.25°	0.67°
O(5) C(1) C(2)	112.87	0.70	O(5') C(1') C(2')	110.28	0.68
O(1) C(1) C(2)	106.73	0.68	O(1) C(1') C(2')	108.31	0.68
C(1) C(2) O(2)	113.14	0.71	C(1') C(2') O(2')	108.13	0.67
C(1) C(2) C(3)	111.45	0.70	C(1') C(2') C(3')	110.82	0.69
O(2) C(2) C(3)	111.25	0.68	O(2') C(2') C(3')	110.29	0.66
C(2) C(3) O(3)	109.54	0.68	C(2') C(3') O(3')	112.49	0.68
C(2) C(3) C(4)	105.64	0.68	C(2') C(3') C(4')	103.88	0.66
O(3) C(3) C(4)	112.86	0.69	O(3') C(3') C(4')	114.51	0.69
C(3) C(4) O(4)	110.03	0.67	C(3') C(4') O(4')	111.81	0.67
C(3) C(4) C(5)	111.54	0.70	C(3') C(4') C(5')	111.36	0.69
O(4) C(4) C(5)	107.34	0.67	O(4') C(4') C(5')	107.84	0.67
C(4) C(5) C(6)	109.43	0.71	C(4') C(5') C(6')	109.81	0.72
C(4) C(5) O(5)	111.89	0.68	C(4') C(5') O(5')	111.60	0.68
C(6) C(5) O(5)	107.95	0.67	C(6') C(5') O(5')	107.48	0.68
C(5) O(5) C(1)	110.01	0.61	C(5') O(5') C(1')	112.29	0.62
C(4) O(4) C(7)	108.84	0.64	C(4') O(4') C(7')	109.98	0.64
O(4) C(7) C(8)	106.06	0.76	O(4') C(7') C(8')	108.00	0.76
O(4) C(7) O(6)	111.41	0.73	O(4') C(7') O(6')	109.72	0.69
C(8) C(7) O(6)	106.88	0.78	C(8') C(7') O(6')	107.85	0.76
C(7) O(6) C(6)	112.55	0.70	C(7') O(6') C(6')	112.68	0.68
O(6) C(6) C(5)	106.95	0.72	O(6') C(6') C(5')	107.87	0.72
C(1) O(1) C(1')	114.99	0.63			

The outstanding feature of the list of bond lengths is that the bonds parallel to C(1) - C(2) and C(1') - C(2') are shorter than expected by about 1.8 estimated standard deviations on average. The other bonds are rather longer than expected, except those in the glucosidic linkage. The short bonds are those which lie most closely parallel to b. The bond angles which are most nearly perpendicular to b are smaller than expected, by almost 5 estimated standard deviations, and the others are too large. No other correlation between bond lengths or angles and their geometry was found.

It is apparent that the observed intensity data contain some systematic error or errors. The rescaling and re-weighting effected towards the end of the refinement had not affected these anomalies significantly. They may have arisen due to absorption effects, caused by the crystal specimen not being exactly circular in cross-section. Since the bulk of the intensity data was collected with the crystal rotating about the y axis, any such absorption error would be serious. It was, however, possible that the error lay in the assumption, which was made in calculating the structure factors, that each atom was vibrating independently of all the other atoms. This was a crude approximation, since much of the molecule is clearly free to "waggle". Since it was known that the intensity data were not very accurate, it was decided that there was little point in investigating this possibility, which in any case lay far beyond the intended scope of this thesis.

It would have been simple to apply an empirical correction to the bond lengths and angles. Since the cause of the observed discrepancies was unknown, it was felt that this would have been unjustified. Had this

correction been applied, then the C(1) - O(1) and C(5) - O(5) bonds in both rings would have been of roughly normal length, whereas the C(1) - O(5) bonds would both have been significantly shorter than average. This agrees well with the results for the second ring of ∝,∝-trehalose, i.e. that in which O(5') did not participate in a hydrogen bond. The remaining significant feature of the table of bond lengths is that the bonds to O(6') are both longer than the corresponding bonds to O(6). This may be due to the fact that O(6') acts as an acceptor in a hydrogen bond.

The large systematic errors in the list of bond angles precludes any meaningful discussion of variations round the pyranose ring, in order to investigate any strain due to the closure of the second ring. The mean internal bond angles in the glucose rings were 110.6° and 110.1° respectively. The corresponding angles for the new rings were 109.5° and 109.7°. The largest differences between corresponding bond angles in the two residues concerned atoms O(2) and O(3) and their counterparts, so that it was concluded that the pattern of hydrogen bonding was responsible.

A NOTE ON DIDEOXY TREHALOSE

The sample sent by Dr. Birch contained two distinct forms of crystals, long needles and compact polyhedra. Both showed clear extinctions when viewed between crossed polarisers. Their equivalence was demonstrated by photography using the 10 cm diameter normal beam Weissenberg camera. The symmetry of the diffraction pattern obtained showed that the crystals were of orthorhombic symmetry. The only systematically absent reflections were I(h00) and I(0k0) for odd values of h and k respectively. The space group was therefore $P2_12_12$, number 18 (International Tables, vol I).

The approximate lattice parameters were found to be:

$$a = 7.80 \text{ Å}$$
$$b = 18.96$$
$$c = 11.04$$

It was not possible to measure the density accurately, the estimates ranged from 1.36 to 1.42 $g.cm^{-3}$. This density corresponds to one or two molecules of water of crystallisation per $C_{12}H_{22}O_9$ molecule. Chemical analysis was also ambiguous (G. G. Birch, 1966).

An attempt was made to collect intensity data for this derivative but the small size of the crystals necessitated the use of very long exposure times. The crystals were so fragile that they fractured before any Weissenberg photographs were completed. This weakness of the crystals suggested that they were probably the monohydrate. It also prevented suitable photographs being obtained for the calculation of accurate cell dimensions.

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I owe a great debt of gratitude to those whose computer programs have been used. The three-dimensional Fourier, intensity statistics and minimum residual programs used were provided by Dr. M. M. Harding who gave much helpful advice concerning their use. The minimum function program was written by Dr. R. Candlin. The two-dimensional Fourier programs used were written by Dr. R. O. Gould who rendered invaluable assistance in the course of the least squares refinements. He and Dr. W. Scott assisted greatly in the application of the Multan method to α,α-trehalose dihydrate. I am grateful to Professor M. M. Woolfson, Dr. P. Main and Dr. G. Germain for the use of the Multan system. I should also like to thank other research students of the X-ray crystallography group for helpful discussions. Thanks are also due to the staff of the Computer Unit of the University of Edinburgh.

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NOTE ON PUBLICATION

Although none of the work described in this thesis has so far been reported in the literature, it is intended that there should be two publications. A paper is being prepared jointly with Dr. D. C. Rohrer and Dr. G. M. Brown, on the three independent determinations of the crystal structure of α,α-trehalose dihydrate. A second paper will presently be written concerning diethylidene trehalose. It is hoped that both papers will be published in Acta Crystallographica.

APPENDIX I

Trehalose Normalised Structure Factors and Phases Deduced by Direct Methods.

h	k	ℓ	E	φ_1	φ_2	φ_3	h	k	ℓ	E	φ_1	φ_2	φ_3
0	2	8	1.86		0°	0°	1	16	3	1.42	-133°	-112°	-81°
0	4	3	2.78	180°	180	180	1	16	6	1.37	-162		-63
0	4	4	1.76	0	0	0	1	17	2	1.56	159	168	171
0	4	6	1.42	0		0	1	17	6	1.70	105	134	73
0	4	7	1.55	0	0	0	1	18	0	1.38	-90		-90
0	4	8	2.25	0	0	0	1	18	5	1.63	-5	12	-29
0	5	1	1.41		-90	-90	1	22	2	1.46	-15	-19	-27
0	5	3	1.88	-90	-90	-90	2	0	3	2.15		-90	90
0	5	8	1.33	-90		-90	2	0	8	1.84	180	0	0
0	5	9	2.03	-90	90	-90	2	0	9	1.62	-90	-90	-90
0	6	6	1.34	0		0	2	1	6	1.39	57		93
0	7	8	1.58	90	90	90	2	1	9	1.60	86	53	-5
0	9	1	1.70	90	-90	90	2	3	1	2.54	-83	-34	-27
0	9	2	2.54	90	90	90	2	3	3	1.74	-102	-110	-18
0	9	5	1.43	-90	-90	-90	2	3	7	1.38	109		107
0	11	3	1.51		-90	-90	2	3	8	1.85	-78	-72	-5
0	11	5	2.09	90	90	90	2	4	0	1.53		180	180
0	12	7	2.02	0	0	0	2	6	3	1.83	179	-171	124
0	14	0	2.18	0	0	0	2	7	8	1.46	-79	-39	6
0	16	0	1.45			180	2	7	9	2.01	-61	-65	-11
0	16	2	1.77	180	180	180	2	8	4	1.48	-159	-95	-101
0	17	1	3.14	90	90	90	2	8	7	1.49	167	113	168
0	17	6	2.34		-90	-90	2	8	8	2.40	-175	-158	148
0	18	5	1.47	180		180	2	8	9	2.09	-165	-177	-136
0	18	6	1.61	0	180	0	2	9	1	1.84	85	60	55
0	21	2	1.69	-90	-90	-90	2	9	7	1.41	-118	-113	-37
1	1	7	2.31	-95	-109	-155	2	9	8	2.57	92	125	32
1	3	0	1.49		-90	-90	2	12	2	1.83	70	-61	127
1	5	0	2.00	90	90	90	2	12	6	1.59	-154	-129	-125
1	6	3	1.54	-72	-31	-55	2	13	3	1.53	119	156	146
1	7	1	1.52	-37	-71	-19	2	13	5	2.27	89	116	80
1	7	8	1.41	-10		23	2	14	2	1.83	130	113	120
1	8	1	2.13	-172	-154	-160	2	14	3	1.74	-11	9	67
1	8	9	2.38	-164	68	-90	2	16	1	1.36	88		63
1	9	0	1.49	90	90	90	2	20	2	1.38	-18		45
1	9	3	1.49	-93	-94	-99	3	0	1	1.40		-90	90
1	9	8	1.42	91	126	-8	3	2	6	1.92	64	6	43
1	12	2	2.53	-6	-53	-50	3	3	5	1.49	-50	-51	-105
1	13	2	2.21	44	84	50	3	3	6	1.50	75	112	26
1	16	2	1.56	6	-68	-3	3	4	0	1.75	90	90	-90

h	k	l	E	φ_1	φ_2	φ_3
3	5	2	1.50	-69		169
3	5	3	1.51	124	62	159
3	7	9	1.73	-83	-66	-71
3	8	8	1.85	-151	149	176
3	9	7	1.36	173		-104
3	11	8	1.51	159		102
3	13	1	1.51	-100	-109	-145
3	13	3	2.00	-92	-121	-75
3	13	4	1.76	-88	-77	-91
3	14	2	1.44	-97	-46	-87
3	14	3	1.68	145	-165	-132
3	14	4	1.35	154		-150
3	15	3	1.60		-26	-113
3	16	5	1.52	-16	-21	42
3	17	0	2.08	-90	-90	-90
3	18	1	1.49	169	132	144
3	20	1	1.42	2		-22
3	22	1	1.84	176	-164	-131
4	0	1	1.78	-90	-90	-90
4	0	2	1.41		0	0
4	1	3	1.69	-131	134	-172
4	2	6	1.48	180	160	-170
4	3	6	1.76	5	88	34
4	4	3	1.76	-13	10	-57
4	4	5	2.13	-80	-26	-114
4	5	2	1.82	-88	-95	-88
4	5	5	1.79	-80	-87	-79
4	5	8	2.00	93	90	69
4	6	0	2.43	180	180	180
4	6	7	1.73	-144	158	173
4	8	6	1.49		0	93
4	8	8	1.40	68		88
4	9	0	2.14	0	180	0
4	9	5	1.64	89	86	90
4	11	3	1.45	157	114	134
4	11	4	2.10	89	78	73
4	12	2	1.37	32		94
4	12	3	1.63	10	2	37
4	12	6	1.58	178	130	176
4	13	3	2.29		58	150
4	13	4	2.41	-30	-78	-23
4	14	0	1.34	180		180
4	17	3	2.20	66	91	92
4	17	6	1.37	-62		-42
4	19	4	1.44	-104		-89
4	20	0	1.88	180	180	180
4	22	1	1.48	-19	-20	8
5	0	2	3.65	0	0	0
5	0	8	1.99	180	180	180
5	1	1	1.57	-69	154	-46
5	1	5	1.81	-130	-124	-175
5	1	6	1.51	57	45	49
5	2	6	2.28	109	173	159
5	3	3	1.44	118	102	123
5	3	6	1.93	-89	-167	-68
5	4	5	2.60	-176	178	-167
5	5	5	2.06	-44	-126	-102
5	5	7	1.81	26	-39	23
5	6	4	1.80	174	-176	169
5	6	5	2.12	-7	-12	-52
5	7	6	1.65	-87	-61	-49
5	7	7	1.77	-52	89	-38
5	7	8	2.20	-42	-103	-89
5	8	3	1.63	-175	-163	176
5	8	5	1.89	-171	-171	-147
5	9	4	1.72	84	63	67
5	10	3	1.58	9	34	84
5	10	7	1.91	-13	4	-26
5	10	8	2.31	-179	161	156
5	11	3	1.95	-89	-75	-63
5	11	4	1.57	-88	-120	-90
5	12	3	1.53	168	-179	154
5	13	7	1.60	-91	-110	-66
5	15	0	2.37	-90	-90	-90
5	16	4	2.14	-168	-162	-121
5	17	1	1.57	116	90	97
5	17	3	1.82	95	102	92
5	18	0	1.39	90		90
5	18	4	1.70	-32	-15	-102
6	0	1	2.20	-90	-90	-90
6	1	2	1.70	102	155	117
6	1	5	2.41	89	78	42
6	1	6	1.71	173	32	-116
6	1	8	1.48	-71		-137
6	2	2	1.79	32	37	21
6	2	6	1.61	-2	35	-2
6	3	2	2.01	-97	-60	-47
6	3	6	1.83	-19	-80	-40
6	4	0	1.59	0		0
6	8	3	2.82	-178	-140	-159
6	13	4	1.69	50	87	34
6	13	5	1.52	-95	-85	-71
6	15	4	1.70	-116	-70	-125
6	16	2	1.36	18		-11
6	16	3	1.79		92	104
6	17	2	1.40	-80		-51
6	18	0	1.48		180	0
6	18	3	1.71	-176	-136	148
6	19	4	1.53	101	82	136
6	20	2	1.36	-22		-42

h	k	ℓ	E	φ_1	φ_2	φ_3
6	21	1	1.43	-64°		-60°
7	0	1	1.82	-90	90°	-90
7	0	6	2.06	0	180	180
7	2	2	1.54	-11	-18	-4
7	3	1	1.48	-97	-163	-147
7	3	3	1.42	-84	-46	-53
7	4	6	2.14	113	-163	136
7	5	0	1.50		-90	90
7	5	2	1.50	37	9	26
7	5	5	1.78	10	7	-25
7	6	7	1.33	-174		-63
7	7	4	1.78	83	43	91
7	8	2	1.40	47		87
7	8	3	1.44	42	88	168
7	8	6	1.45		-112	-63
7	9	3	1.70	1	33	2
7	9	4	1.95	-83	173	102
7	11	7	1.47	-123	-136	-85
7	14	0	2.93	-90	-90	-90
7	15	3	1.44	88	128	65
7	16	3	1.34	40		-26
7	17	2	1.40	-32	175	-15
7	17	5	1.68		-98	-85
7	18	1	1.61	-171	-130	-156
7	19	0	1.80	90	90	90
7	19	2	1.47	63	-29	-32
7	19	3	1.54	93	76	73
8	0	8	1.42			180
8	2	5	1.37	-54		113
8	3	7	2.21		-20	-33
8	3	8	1.59	93	135	34
8	4	5	1.42	54	44	37
8	4	8	1.84	-38	-17	11
8	5	7	1.68	-90	-44	-31
8	7	3	1.47	122		9
8	8	2	1.52	66	6	92
8	8	3	1.60	177	103	-159
8	11	7	1.41	88	66	94
8	12	3	1.62	-18	26	8
8	12	5	1.36	-59		3
8	13	3	1.35	-100		-71
8	14	0	1.42		180	180
8	14	5	1.43	154		-109
8	16	1	1.34	96		97
8	16	5	1.36	69		81
8	17	2	1.49	-91	-53	-71
8	17	4	1.51	-100	-92	-125
9	2	8	1.58	178	159	-161
9	5	0	3.20	90	90	90
9	5	5	1.45	-30	5	23
9	5	6	1.70	-91°	-151°	-149°
9	6	0	1.71	90	90	90
9	7	1	1.51	-124	-77	-134
9	8	1	1.40	-177	-176	169
9	8	2	1.50	123	-114	131
9	9	3	2.16	-82	-97	-96
9	11	2	1.85	-73	-91	-87
9	11	5	1.57	136	143	-177
9	12	1	1.50	-174	-169	-148
9	12	5	1.60	-10	109	54
9	13	2	1.41	134	95	100
9	15	2	1.66	-95	-112	-141
9	17	1	2.36	-140	-103	-125
9	17	3	1.71	-133	117	144
10	0	0	2.07	180	180	180
10	1	0	1.84		180	180
10	1	1	1.78	78	111	62
10	1	3	1.78	40	73	-5
10	2	0	2.53	0	0	0
10	3	0	1.48	0	0	0
10	3	1	2.33	-87	-65	-69
10	4	1	1.89	-91	-159	-136
10	4	2	1.41	-170	-176	-176
10	4	3	1.39	-5		-19
10	5	0	1.50	0	0	0
10	5	1	1.51	137	145	-152
10	5	3	1.35	143		76
10	6	3	1.56	178	-176	173
10	6	6	1.64		-175	-161
10	6	7	2.66	3	-1	-64
10	8	0	1.44	0		0
10	8	2	1.69	130	160	127
10	9	6	1.54	79	64	28
10	10	1	1.59	-164	-170	-105
10	11	2	1.87	77	6	78
10	13	3	1.50		-111	-88
10	14	0	1.70	180	180	180
10	14	3	1.34	-17		-33
10	15	1	1.74	93	113	105
10	16	0	1.50	0	0	0
10	17	2	1.39	78		61
11	1	0	1.77	-90	-90	-90
11	2	1	2.26	-169	129	159
11	2	2	1.73	180	169	-151
11	2	5	1.44	-8	41	-19
11	4	0	2.32		90	90
11	5	1	1.35	-52		-3
11	6	1	1.32	-177		160
11	6	6	1.77	-131	-67	-147
11	7	0	2.37	90	90	90

h	k	ℓ	E	φ_1	φ_2	φ_3
11	8	0	1.54	90	90	90
11	8	1	2.03	7	51	69
11	8	2	1.33	116		44
11	8	6	1.39	-131		138
11	9	0	1.59	-90	-90	-90
11	9	1	1.44	-27	32	-2
11	9	2	1.65	-110	-146	-135
11	9	3	1.38	76		34
11	11	3	1.34	-96		-136
11	12	2	1.73	171	121	107
11	12	3	1.78	-44	-52	-46
11	14	2	1.67	-13	-75	-51
12	0	1	1.53	90		90
12	1	0	1.49	0	0	0
12	1	1	1.55	-69	-38	-22
12	2	3	1.39	-17		-19
12	2	4	1.71	-40	-50	-20
12	4	4	1.89	-46	31	-48
12	7	2	1.73	-115	-135	-83
12	7	4	1.50	-73		-82
12	8	1	1.78		-18	-53
12	8	3	1.40		-1	18
12	8	4	1.90	27	62	53
13	1	0	1.60	-90	-90	-90
13	4	0	1.69		-90	90
13	4	4	1.35	89		115
13	6	3	2.34	-92	-141	-112
13	7	2	1.85		167	129
13	8	4	2.10	61	-4	79
13	9	3	1.77	76	114	30
14	1	0	1.81	0	0	0
14	3	3	1.44	-121	-37	-105
14	4	1	1.97	-169	-24	106
14	5	2	1.45	99	95	84
14	5	3	2.08	99	153	-170
14	5	4	1.41	91	-44	8
14	6	3	1.61	5	7	16
14	7	3	1.89	-138	-90	-110
15	1	1	1.53	116	-17	90
15	2	2	1.50	7	-8	6

E values were obtained using the K-curve program;

φ_1 = phase obtained in the original determination;

φ_2 = phase obtained by the Multan system;

φ_3 = phase computed in the final refinement of the atomic parameters.

APPENDIX II

Independently Measured Cell Dimensions of Trehalose.

a	b	c	
12.233 Å	17.889 Å	7.596 Å	(a)
12.230	17.902	7.598	(b)
12.230	17.890	7.5946	(c)

The present results are indicated by (a). They were deduced from measurements of Weissenberg photographs which had been exposed at about 18°C. (b) and (c) show the results of Dr. G. M. Brown and Dr. D. C. Rohrer respectively. These were obtained by diffractometric techniques at temperatures between 20 and 25°C.

APPENDIX III

Comparison of Bond Lengths and Angles Obtained in the Independent Studies of Trehalose.

Atoms	Edinburgh		Oak Ridge		Pittsburgh	
	Length	E.S.D.	Length	E.S.D.	Length	E.S.D.
C(1) - C(2)	1.5159	0.0046 Å	1.5214	0.0027 Å	1.5236	0.0040 Å
C(2) - C(3)	1.5262	0.0046	1.5238	0.0028	1.5242	0.0038
C(3) - C(4)	1.5300	0.0046	1.5214	0.0027	1.5365	0.0040
C(4) - C(5)	1.5323	0.0044	1.5265	0.0026	1.5283	0.0036
C(5) - C(6)	1.5268	0.0045	1.5183	0.0027	1.5235	0.0039
C(1) - O(1)	1.4149	0.0037	1.4155	0.0022	1.4154	0.0031
C(1) - O(5)	1.4212	0.0040	1.4196	0.0023	1.4224	0.0035
C(5) - O(5)	1.4363	0.0038	1.4342	0.0022	1.4283	0.0031
C(2) - O(2)	1.4218	0.0041	1.4234	0.0024	1.4123	0.0036
C(3) - O(3)	1.4177	0.0042	1.4191	0.0026	1.4118	0.0034
C(4) - O(4)	1.4115	0.0040	1.4213	0.0025	1.4207	0.0032
C(6) - O(6)	1.4149	0.0040	1.4163	0.0024	1.4226	0.0035
C(1') - C(2')	1.5356	0.0045	1.5343	0.0026	1.5277	0.0039
C(2') - C(3')	1.5289	0.0045	1.5165	0.0026	1.5188	0.0040
C(3') - C(4')	1.5134	0.0046	1.5173	0.0027	1.5260	0.0039
C(4') - C(5')	1.5217	0.0043	1.5259	0.0025	1.5306	0.0036
C(5') - C(6')	1.5197	0.0047	1.5126	0.0028	1.5196	0.0040
C(1') - O(1)	1.4185	0.0038	1.4205	0.0022	1.4266	0.0032
C(1') - O(5')	1.3914	0.0038	1.4061	0.0022	1.4085	0.0031
C(5') - O(5')	1.4356	0.0040	1.4325	0.0023	1.4255	0.0035
C(2') - O(2')	1.4216	0.0040	1.4202	0.0024	1.4262	0.0033
C(3') - O(3')	1.4214	0.0041	1.4265	0.0023	1.4164	0.0034
C(4') - O(4')	1.4296	0.0042	1.4327	0.0025	1.4191	0.0036
C(6') - O(6')	1.4268	0.0042	1.4231	0.0026	1.4290	0.0035

Atoms	Edinburgh		Oak Ridge		Pittsburgh	
	Length	E.S.D.	Length	E.S.D.	Length	E.S.D.
C(1) - H(1)	0.919 Å	0.057 Å	0.990 Å	0.022 Å	0.960 Å	0.031 Å
C(2) - H(2)	0.989	0.057	0.991	0.022	0.888	0.035
C(3) - H(3)	0.997	0.057	0.965	0.021	1.053	0.036
C(4) - H(4)	0.976	0.057	0.972	0.024	0.987	0.033
C(5) - H(5)	1.005	0.058	0.929	0.024	1.106	0.032
C(6) - H(6)	1.073	0.061	0.995	0.026	1.042	0.036
C(6) - H(7)	1.036	0.062	0.952	0.027	1.058	0.035
O(2) - H(8)	1.012	0.059	0.754	0.034	0.688	0.037
O(3) - H(9)	0.819	0.062	0.744	0.026	0.827	0.042
O(4) - H(10)	0.894	0.061	0.652	0.032	0.910	0.035
O(6) - H(11)	0.931	0.061	0.783	0.035	0.800	0.036
C(1') - H(12)	0.867	0.064	0.934	0.025	1.007	0.037
C(2') - H(13)	0.961	0.060	0.905	0.025	0.990	0.035
C(3') - H(14)	0.932	0.059	0.940	0.023	1.025	0.033
C(4') - H(15)	0.999	0.059	0.976	0.024	0.960	0.035
C(5') - H(16)	0.974	0.059	0.962	0.021	0.987	0.033
C(6') - H(17)	0.955	0.058	0.980	0.025	0.845	0.036
C(6') - H(18)	1.022	0.059	1.005	0.027	1.075	0.035
O(2') - H(19)	1.012	0.059	0.815	0.036	1.013	0.036
O(3') - H(20)	0.865	0.064	0.780	0.028	0.787	0.040
O(4') - H(21)	0.935	0.057	0.702	0.040	0.849	0.033
O(6') - H(22)	0.975	0.058	0.744	0.028	1.033	0.036
O(W1) - H(23)	0.879	0.059	0.742	0.034	0.741	0.045
O(W1) - H(24)	0.842	0.059	0.820	0.035	0.824	0.043
O(W2) - H(25)	0.837	0.058	0.775	0.030	0.913	0.040
O(W2) - H(26)	0.802	0.061	0.733	0.035	0.860	0.043

H	K	L	FOBS	FCAL	PHASE
0	2	0	163	160	0
0	4	0	646	707	0
0	6	0	529	541	0
0	8	0	107	115	180
0	10	0	113	110	0
0	12	0	205	203	0
0	14	0	580	621	0
0	16	0	308	314	180
0	18	0	124	123	0
0	20	0	93	94	0
0	22	0	77	75	0
1	1	0	271	253	90
1	2	0	185	173	90
1	3	0	824	858	-90
1	4	0	498	527	-90
1	5	0	981	1049	90
1	6	0	176	176	90
1	7	0	231	238	-90
1	8	0	207	214	90
1	9	0	483	512	90
1	10	0	192	178	-90
1	11	0	54	49	-90
1	12	0	35	2	-90
1	13	0	111	98	-90
1	14	0	82	83	-90
1	15	0	88	82	90
1	16	0	123	124	-90
1	17	0	89	89	-90
1	18	0	165	175	-90
1	19	0	33	24	-90
1	20	0	0	4	-90
1	21	0	22	17	-90
1	22	0	22	23	-90
2	23	0	27	37	90
2	0	0	530	555	0
2	1	0	409	415	180
2	2	0	632	668	0
2	3	0	418	416	0
2	4	0	730	704	180
2	5	0	574	586	0
2	6	0	275	284	180
2	7	0	507	495	0
2	8	0	269	245	180
2	9	0	379	395	0
2	10	0	289	299	180
2	11	0	299	295	0
2	12	0	43	39	-180
2	13	0	104	96	180
2	14	0	128	118	180
2	15	0	0	10	-180
2	16	0	152	160	180
2	17	0	128	130	0
2	18	0	0	8	0
2	19	0	69	65	0
2	20	0	73	79	0
2	21	0	40	38	0
2	22	0	85	85	180
3	1	0	491	505	90
3	2	0	85	80	90
3	3	0	131	140	-90
3	4	0	769	774	-90
3	5	0	192	181	-90
3	6	0	170	168	90
3	7	0	113	109	-90
3	8	0	14	21	-90
3	9	0	183	144	90
3	10	0	496	495	90
3	11	0	191	183	90
3	12	0	219	235	-90
3	13	0	152	152	90
3	14	0	123	118	90
3	15	0	141	140	90
3	16	0	65	66	-90
3	17	0	262	271	-90
3	18	0	106	96	-90
3	19	0	47	43	-90
3	20	0	103	99	90
3	21	0	100	96	-90
3	22	0	63	57	-90
4	0	0	805	764	180
4	1	0	195	196	180
4	2	0	320	339	0
4	3	0	298	302	0
4	4	0	252	234	180
4	5	0	316	300	180
4	6	0	457	450	180
4	7	0	430	415	0
4	8	0	399	387	180
4	9	0	560	613	0
4	10	0	177	178	0
4	11	0	265	265	180
4	12	0	174	195	0
4	13	0	49	44	180
4	14	0	221	239	180
4	15	0	115	112	-180
4	16	0	124	116	0
4	17	0	61	77	0
4	18	0	44	41	0
4	19	0	63	56	180
4	20	0	162	158	180

H	K	L	FOBS	FCAL	PHASE
4	21	0	49	47	0
5	1	0	456	444	-90
5	2	0	349	363	-90
5	3	0	321	320	-90
5	4	0	35	23	-90
5	5	0	289	240	-90
5	6	0	104	109	-90
5	7	0	29	18	-90
5	8	0	160	157	90
5	9	0	195	193	-90
5	10	0	35	27	-90
5	11	0	124	120	-90
5	12	0	123	136	-90
5	13	0	0	8	90
5	14	0	61	62	-90
5	15	0	330	347	-90
5	16	0	0	8	90
5	17	0	73	67	90
5	18	0	142	146	90
5	19	0	100	99	-90
5	20	0	0	11	90
5	21	0	25	17	90
6	0	0	55	64	-180
6	1	0	43	47	0
6	2	0	143	138	180
6	3	0	78	73	180
6	4	0	488	470	0
6	5	0	267	240	180
6	6	0	138	141	0
6	7	0	48	48	0
6	8	0	107	104	0
6	9	0	102	100	0
6	10	0	259	279	0
6	11	0	191	181	180
6	12	0	195	212	180
6	13	0	63	67	180
6	14	0	57	58	0
6	15	0	56	66	0
6	16	0	64	75	180
6	17	0	73	77	0
6	18	0	141	141	0
6	19	0	31	41	180
6	20	0	85	87	0
6	21	0	29	29	0
7	1	0	201	219	90
7	2	0	370	358	-90
7	3	0	239	243	90
7	4	0	78	73	90
7	5	0	378	372	90
7	6	0	57	60	-90
7	7	0	297	291	-90
7	8	0	183	182	90
7	9	0	165	181	90
7	10	0	90	96	-90
7	11	0	0	14	-90
7	12	0	150	150	-90
7	13	0	27	28	90
7	14	0	379	396	-90
7	15	0	0	8	90
7	16	0	0	10	-90
7	17	0	85	89	-90
7	18	0	52	44	90
7	19	0	142	145	90
7	20	0	31	31	-90
8	0	0	412	398	0
8	1	0	279	294	180
8	2	0	22	16	180
8	3	0	179	189	180
8	4	0	35	19	180
8	5	0	196	200	0
8	6	0	0	14	180
8	7	0	47	41	180
8	8	0	49	53	-180
8	9	0	93	98	180
8	10	0	145	154	180
8	11	0	179	187	0
8	12	0	118	125	180
8	13	0	46	48	0
8	14	0	166	179	180
8	15	0	109	110	180
8	16	0	48	39	0
8	17	0	46	54	0
8	18	0	75	77	180
8	19	0	27	19	-180
9	1	0	111	113	90
9	2	0	102	96	90
9	3	0	27	22	90
9	4	0	136	139	90
9	5	0	596	617	90
9	6	0	305	320	90
9	7	0	215	228	90
9	8	0	79	75	90
9	9	0	153	150	90
9	10	0	37	34	-90
9	11	0	59	54	90
9	12	0	133	141	-90
9	13	0	76	70	-90
9	14	0	130	142	-90
9	15	0	22	26	90
9	16	0	40	34	90

H	K	L	FOBS	FCAL	PHASE
9	17	0	33	26	90
9	18	0	78	79	90
10	0	0	513	513	180
10	1	0	322	324	180
10	2	0	438	417	0
10	3	0	251	260	0
10	4	0	111	103	180
10	5	0	240	257	0
10	6	0	63	56	0
10	7	0	0	7	180
10	8	0	201	214	0
10	9	0	37	27	0
10	10	0	62	64	180
10	11	0	55	52	0
10	12	0	33	40	180
10	13	0	125	128	0
10	14	0	158	163	180
10	15	0	54	58	180
10	16	0	117	123	0
10	17	0	0	14	0
11	1	0	262	254	-90
11	2	0	132	128	-90
11	3	0	56	65	-90
11	4	0	327	346	90
11	5	0	133	139	-90
11	6	0	73	77	90
11	7	0	300	325	90
11	8	0	185	186	90
11	9	0	182	190	-90
11	10	0	55	48	90
11	11	0	37	30	-90
11	12	0	22	16	90
11	13	0	22	15	90
11	14	0	35	42	90
11	15	0	0	10	-90
11	16	0	0	12	-90
12	0	0	77	76	0
12	1	0	187	184	0
12	2	0	94	86	180
12	3	0	55	55	180
12	4	0	0	0	180
12	5	0	73	66	0
12	6	0	81	85	180
12	7	0	107	114	0
12	8	0	40	42	0
12	9	0	79	87	0
12	10	0	88	102	0
12	11	0	57	56	0
12	12	0	25	25	0
12	13	0	46	37	180
12	14	0	40	43	0
13	1	0	171	170	-90
13	2	0	0	2	-90
13	3	0	74	88	-90
13	4	0	173	175	90
13	5	0	114	113	90
13	6	0	0	4	-90
13	7	0	71	64	90
13	8	0	56	48	-90
13	9	0	107	112	90
13	10	0	61	63	-90
13	11	0	54	51	-90
13	12	0	48	53	90
13	13	0	57	69	90
14	0	0	44	36	180
14	1	0	163	156	0
14	2	0	31	32	180
14	3	0	44	43	180
14	4	0	106	104	180
14	5	0	0	9	180
14	6	0	0	12	180
14	7	0	56	53	0
14	8	0	59	61	0
14	9	0	22	17	-180
14	10	0	48	50	0
15	1	0	95	91	-90
15	2	0	60	54	90
15	3	0	81	81	90
15	4	0	67	65	-90
15	5	0	81	82	-90
15	6	0	31	36	-90
15	7	0	35	43	-90
0	1	1	564	633	-90
0	2	1	588	617	180
0	3	1	598	649	90
0	4	1	502	506	0
0	5	1	663	710	-90
0	6	1	573	588	180
0	7	1	344	352	90
0	8	1	239	256	180
0	9	1	541	566	90
0	10	1	108	100	180
0	11	1	281	267	-90
0	12	1	240	255	180
0	13	1	97	92	90
0	14	1	214	211	180
0	15	1	125	130	90
0	16	1	55	55	0
0	17	1	415	426	90
0	18	1	41	21	180

H	K	L	FOBS	FCAL	PHASE
0	19	1	0	6	-90
0	20	1	74	66	0
0	21	1	73	62	90
0	22	1	81	70	180
1	0	1	742	624	90
1	1	1	442	447	-169
1	2	1	636	646	81
1	3	1	417	403	155
1	4	1	413	402	-121
1	5	1	307	309	134
1	6	1	394	389	-40
1	7	1	586	582	-19
1	8	1	744	784	-160
1	9	1	291	268	65
1	10	1	101	93	146
1	11	1	342	335	-39
1	12	1	139	138	102
1	13	1	197	203	-32
1	14	1	129	129	-4
1	15	1	113	115	78
1	16	1	136	139	93
1	17	1	106	106	-55
1	18	1	78	70	-7
1	19	1	59	49	62
1	20	1	54	47	41
1	21	1	104	97	19
1	22	1	95	89	149
2	0	1	650	691	-90
2	1	1	161	171	-32
2	2	1	596	607	12
2	3	1	1266	1460	-27
2	4	1	296	297	90
2	5	1	450	473	-43
2	6	1	89	92	-45
2	7	1	279	255	118
2	8	1	170	155	-175
2	9	1	558	569	55
2	10	1	187	186	-141
2	11	1	136	124	-8
2	12	1	149	155	-143
2	13	1	204	205	-168
2	14	1	107	104	-104
2	15	1	118	122	0
2	16	1	195	196	63
2	17	1	100	104	54
2	18	1	99	98	30
2	19	1	91	89	31
2	20	1	68	62	95
2	21	1	103	89	-163
2	22	1	84	79	60
3	0	1	688	736	90
3	1	1	565	599	175
3	2	1	433	442	-155
3	3	1	307	306	-113
3	4	1	507	489	-179
3	5	1	512	511	167
3	6	1	143	154	-121
3	7	1	253	234	138
3	8	1	364	361	-175
3	9	1	235	227	89
3	10	1	61	53	178
3	11	1	71	65	45
3	12	1	174	164	30
3	13	1	286	279	-145
3	14	1	127	121	70
3	15	1	149	146	-144
3	16	1	104	104	-101
3	17	1	49	44	-147
3	18	1	106	105	144
3	19	1	76	72	152
3	20	1	126	118	-22
3	21	1	22	23	-115
3	22	1	128	118	-131
4	0	1	774	836	-90
4	1	1	439	451	-118
4	2	1	238	234	23
4	3	1	282	282	-8
4	4	1	211	205	41
4	5	1	357	355	47
4	6	1	231	220	-31
4	7	1	65	53	115
4	8	1	158	157	-44
4	9	1	226	215	-102
4	10	1	174	177	-62
4	11	1	79	69	177
4	12	1	96	95	-83
4	13	1	117	99	-163
4	14	1	150	151	-56
4	15	1	43	32	143
4	16	1	141	141	81
4	17	1	96	89	14
4	18	1	40	37	-180
4	19	1	63	55	156
4	20	1	0	6	0
4	21	1	44	40	-45
4	22	1	99	99	8
5	0	1	472	469	-90
5	1	1	591	581	-46
5	2	1	491	491	0
5	3	1	311	294	5

H	K	L	FOBS	FCAL	PHASE
5	4	1	146	165	-178
5	5	1	283	256	135
5	6	1	55	43	-159
5	7	1	51	45	142
5	8	1	75	66	47
5	9	1	246	231	-6
5	10	1	116	112	158
5	11	1	263	271	44
5	12	1	160	164	130
5	13	1	65	78	-84
5	14	1	192	200	-10
5	15	1	55	37	-90
5	16	1	0	11	-30
5	17	1	176	181	97
5	18	1	57	49	115
5	19	1	44	42	-91
5	20	1	77	72	-130
5	21	1	86	80	35
6	0	1	719	730	-90
6	1	1	275	264	-88
6	2	1	51	40	164
6	3	1	362	357	-135
6	4	1	273	287	1
6	5	1	184	175	83
6	6	1	93	86	14
6	7	1	37	29	-160
6	8	1	216	204	180
6	9	1	83	86	16
6	10	1	100	93	-147
6	11	1	150	141	111
6	12	1	210	220	-12
6	13	1	150	165	54
6	14	1	73	69	-84
6	15	1	133	130	-47
6	16	1	132	135	114
6	17	1	0	2	21
6	18	1	61	52	-13
6	19	1	41	36	156
6	20	1	31	34	-167
6	21	1	95	102	-80
7	0	1	307	296	-90
7	1	1	115	131	-28
7	2	1	199	203	-75
7	3	1	193	175	-147
7	4	1	344	334	-151
7	5	1	204	200	-135
7	6	1	64	67	-74
7	7	1	91	73	168
7	8	1	148	146	-26
7	9	1	142	134	-7
7	10	1	150	143	-19
7	11	1	64	60	50
7	12	1	157	166	-114
7	13	1	111	110	38
7	14	1	152	156	-110
7	15	1	62	60	-131
7	16	1	65	59	52
7	17	1	96	100	141
7	18	1	113	140	-156
7	19	1	31	30	-89
7	20	1	51	49	34
8	0	1	82	83	90
8	1	1	54	45	-155
8	2	1	233	247	155
8	3	1	114	104	161
8	4	1	55	41	-52
8	5	1	147	154	-138
8	6	1	158	164	161
8	7	1	131	129	-155
8	8	1	209	207	149
8	9	1	94	91	-69
8	10	1	83	83	13
8	11	1	35	32	102
8	12	1	178	180	56
8	13	1	84	83	154
8	14	1	136	140	70
8	15	1	136	136	40
8	16	1	129	130	97
8	17	1	111	111	136
8	18	1	101	103	-175
8	19	1	46	43	-143
9	0	1	218	220	90
9	1	1	25	12	133
9	2	1	123	114	-141
9	3	1	230	230	-156
9	4	1	206	206	166
9	5	1	161	163	174
9	6	1	188	200	48
9	7	1	252	272	-134
9	8	1	221	235	149
9	9	1	94	93	-17
9	10	1	40	46	31
9	11	1	144	146	-34
9	12	1	181	180	-148
9	13	1	117	115	-59
9	14	1	77	77	171
9	15	1	81	88	107
9	16	1	29	29	-143
9	17	1	185	197	-125
9	18	1	38	43	-22

H	K	L	FOBS	FCAL	PHASE
10	0	1	33	22	90
10	1	1	805	809	67
10	2	1	134	150	-36
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10	4	1	307	317	-146
10	5	1	236	241	-152
10	6	1	129	121	-177
10	7	1	78	76	-96
10	8	1	121	111	-45
10	9	1	69	69	-166
10	10	1	134	147	-105
10	11	1	69	90	90
10	12	1	60	58	-47
10	13	1	91	92	-65
10	14	1	76	63	71
10	15	1	145	146	105
10	16	1	90	85	-161
10	17	1	63	72	-126
11	1	1	63	52	90
11	2	1	50	50	67
11	3	1	247	215	159
11	4	1	77	73	15
11	5	1	114	121	111
11	6	1	141	141	-3
11	7	1	172	177	140
11	8	1	61	49	113
11	9	1	241	236	49
11	10	1	164	163	-74
11	11	1	90	95	-174
11	12	1	69	69	27
11	13	1	91	90	-19
11	14	1	91	94	-176
12	0	1	146	147	90
12	1	1	84	84	64
12	2	1	148	144	-42
12	3	1	94	93	-146
12	4	1	124	101	-40
12	5	1	95	94	-108
12	6	1	41	40	157
12	7	1	102	104	-53
12	8	1	60	55	-140
12	9	1	120	115	-48
12	10	1	73	67	-65
12	11	1	0	11	-28
12	12	1	90	85	-54
12	13	1	43	39	32
13	0	1	105	98	-90
13	1	1	102	106	-16
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13	4	1	34	41	154
13	5	1	69	68	-17
13	6	1	99	99	-95
13	7	1	79	76	100
13	8	1	41	40	71
13	9	1	80	88	90
13	10	1	130	106	163
14	11	1	22	22	164
14	12	1	37	37	162
14	0	1	67	66	90
14	1	1	53	51	26
14	2	1	56	51	77
14	3	1	61	77	-116
14	4	1	167	170	106
14	5	1	31	23	-67
14	6	1	77	71	23
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14	8	1	46	49	-25
14	9	1	55	54	61
14	10	1	57	56	78
15	0	1	57	55	-90
15	1	1	113	115	90
15	2	1	36	33	-146
15	3	1	86	94	-124
15	4	1	41	34	-57
15	5	1	67	62	-35
15	6	1	16	14	-47
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0	4	2	126	132	0
0	5	2	557	567	90
0	6	2	233	227	180
0	7	2	404	406	-90
0	8	2	259	276	0
0	9	2	736	749	90
0	10	2	52	52	0
0	11	2	161	164	90
0	12	2	118	111	180
0	13	2	46	57	-90
0	14	2	151	150	0
0	15	2	143	154	90
0	16	2	247	237	180
0	17	2	63	57	-90
0	18	2	38	33	0

H	K	L	FOBS	FCAL	PHASE
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0	20	2	51	48	0
0	21	2	134	117	-90
0	22	2	65	56	0
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1	2	2	845	840	36
1	3	2	312	329	30
1	4	2	198	201	-156
1	5	2	471	472	41
1	6	2	367	369	140
1	7	2	301	296	77
1	8	2	161	146	-59
1	9	2	379	362	110
1	10	2	201	195	-10
1	11	2	278	249	-54
1	12	2	532	571	-50
1	14	2	420	445	50
1	14	2	43	46	-122
1	15	2	80	78	-117
1	16	2	210	225	-3
1	17	2	194	200	171
1	18	2	93	94	-108
1	19	2	96	96	108
1	20	2	100	99	125
1	21	2	54	41	145
1	22	2	102	101	-27
2	0	2	332	332	0
2	1	2	951	968	-63
2	2	2	343	326	-129
2	3	2	179	195	100
2	4	2	160	161	173
2	5	2	74	55	-91
2	6	2	237	234	61
2	7	2	153	148	59
2	8	2	314	314	-114
2	9	2	135	125	85
2	10	2	70	65	96
2	11	2	160	178	173
2	12	2	376	392	127
2	13	2	239	246	-74
2	14	2	306	326	120
2	15	2	125	149	-140
2	16	2	141	152	167
2	17	2	82	88	73
2	18	2	74	71	113
2	19	2	64	59	-87
2	20	2	120	114	45
2	21	2	75	71	128
2	22	2	37	36	-47
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3	1	2	585	581	59
3	2	2	423	421	-86
3	3	2	357	339	-15
3	4	2	356	358	162
3	5	2	542	550	169
3	6	2	393	396	142
3	7	2	131	122	-144
3	8	2	106	108	-58
3	9	2	117	103	73
3	10	2	181	183	-44
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3	12	2	103	101	4
3	13	2	198	199	52
3	14	2	231	237	-87
3	15	2	131	135	53
3	16	2	0	4	54
3	17	2	116	108	-124
3	18	2	94	82	90
3	19	2	59	55	-175
3	20	2	49	20	109
3	21	2	76	72	-46
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4	2	2	378	371	-98
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4	4	2	334	282	28
4	5	2	598	617	-88
4	6	2	338	334	-156
4	7	2	161	146	10
4	8	2	191	179	-113
4	9	2	235	198	-58
4	10	2	109	112	-61
4	11	2	83	86	-176
4	12	2	231	253	94
4	13	2	56	52	126
4	14	2	90	73	117
4	15	2	64	67	-155
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4	19	2	33	31	101
4	20	2	54	44	-45
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5	2	2	193	162	-153
5	3	2	236	183	145
5	4	2	54	49	164
5	5	2	298	267	164
5	6	2	235	233	121
5	7	2	328	330	-118
5	8	2	234	235	-172
5	9	2	152	157	90
5	10	2	150	93	-5
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5	13	2	193	182	-126
5	14	2	186	196	-41
5	15	2	57	47	46
5	16	2	142	143	164
5	17	2	78	74	-73
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5	19	2	83	95	-79
5	20	2	47	42	122
5	21	2	71	70	-68
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6	1	2	502	481	117
6	2	2	519	512	21
6	3	2	567	579	-47
6	4	2	221	212	-20
6	5	2	120	109	82
6	6	2	216	217	10
6	7	2	255	249	-53
6	8	2	86	82	25
6	9	2	167	163	42
6	10	2	165	168	-3
6	11	2	173	174	-145
6	12	2	53	46	-19
6	13	2	65	61	-20
6	14	2	72	69	-162
6	15	2	84	84	-101
6	16	2	146	146	-11
6	17	2	138	145	-51
6	18	2	89	81	-44
6	19	2	56	52	71
6	20	2	97	96	-42
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7	2	2	365	360	-4
7	3	2	124	117	43
7	4	2	89	77	-87
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7	6	2	76	79	-14
7	7	2	106	96	-68
7	8	2	288	270	87
7	9	2	44	33	-74
7	10	2	139	138	133
7	11	2	188	192	42
7	12	2	139	152	-62
7	13	2	37	36	-115
7	14	2	120	124	176
7	15	2	92	91	106
7	16	2	59	48	-62
7	17	2	126	122	-15
7	18	2	87	86	-2
7	19	2	108	103	-32
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8	2	2	184	196	46
8	3	2	150	153	-57
8	4	2	208	216	-118
8	5	2	255	258	-64
8	6	2	230	236	167
8	7	2	120	116	12
8	8	2	258	275	92
8	9	2	151	150	-22
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8	11	2	155	152	115
8	12	2	131	126	-90
8	13	2	155	158	65
8	14	2	59	59	-5
8	15	2	41	37	-83
8	16	2	49	36	-114
8	17	2	123	126	-71
8	18	2	81	78	-70
8	19	2	83	70	-11
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9	1	2	195	158	-171
9	2	2	124	136	-135
9	3	2	137	142	-45
9	4	2	167	166	133
9	5	2	226	226	31
9	6	2	166	171	-157
9	7	2	97	91	-28
9	8	2	123	127	131
9	9	2	91	92	70
9	10	2	66	65	165
9	11	2	228	251	-87
9	12	2	29	26	-71
9	13	2	150	161	100
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9	15	2	149	156	-141
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9	17	2	48	49	-108
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10	12	2	56	56	-28
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10	17	2	93	119	61
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11	7	2	94	88	144
11	8	2	150	153	44
11	9	2	177	177	-135
11	10	2	86	84	-31
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11	12	2	153	151	107
11	13	2	109	116	-152
11	14	2	126	142	-51
11	15	2	49	52	69
12	0	2	93	90	0
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12	7	2	176	179	-83
12	8	2	37	38	-168
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12	11	2	40	36	-55
12	12	2	85	87	-25
12	13	2	84	87	-155
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13	2	2	36	29	177
13	3	2	109	109	99
13	4	2	52	47	147
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13	6	2	86	92	-3
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13	9	2	81	77	138
13	10	2	0	9	-16
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14	2	2	41	32	42
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14	7	2	29	24	34
14	8	2	91	96	-148
14	9	2	25	21	10
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0	10	3	226	224	0
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0	12	3	41	31	-180
0	13	3	223	230	90
0	14	3	74	76	180
0	15	3	123	118	-90
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0	19	3	103	87	-90
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2	9	3	153	159	60
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2	12	3	241	244	96
2	13	3	255	266	146
2	14	3	263	260	67
2	15	3	112	110	155
2	16	3	63	62	-42
2	17	3	136	136	-13
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2	19	3	52	49	123
2	20	3	64	57	95
2	21	3	38	29	-88
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3	6	3	229	215	0
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3	8	3	33	24	25
3	9	3	244	249	167
3	10	3	272	277	93
3	11	3	190	189	14
3	12	3	93	81	89
3	13	3	320	328	-75
3	14	3	240	244	-132
3	15	3	211	215	-113
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4	1	3	47	41	-9
4	2	3	0	14	-23
4	3	3	51	50	-169
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4	6	3	269	263	-90
4	7	3	542	544	-172
4	8	3	194	194	126
4	9	3	110	103	-49
4	10	3	520	535	-57
4	11	3	149	135	-46
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9	10	5	55	47	100
9	11	5	136	136	-177
9	12	5	129	127	54
9	13	5	64	65	179
9	14	5	60	62	-13
10	0	5	51	50	-90
10	1	5	81	71	122
10	2	5	53	49	-80
10	3	5	46	28	124
10	4	5	127	134	41
10	5	5	97	99	156
10	6	5	60	53	-49
10	7	5	102	112	158
10	8	5	102	87	-156
10	9	5	29	24	105
10	10	5	100	95	90
10	11	5	65	54	-26
10	12	5	56	58	119
10	13	5	0	2	90
11	0	5	57	60	-66
11	1	5	137	133	-19
11	2	5	52	51	-42
11	3	5	22	29	72
11	4	5	0	5	18
11	5	5	33	41	-166
11	6	5	64	55	-7
11	7	5	69	83	169
11	8	5	46	44	15
11	9	5	35	34	51
11	10	5	47	51	-26
11	11	5	47	48	-90
12	0	5	85	82	133
12	1	5	65	76	-75
12	2	5	41	39	-107
12	3	5	80	72	-153
12	4	5	65	75	45
12	5	5	51	48	143
12	6	5	77	70	-77
12	7	5	44	36	126
12	8	5	46	47	-31
13	0	5	61	67	90
13	1	5	31	30	-13
13	2	5	60	61	15
13	3	5	49	52	72
13	4	5	40	34	-174
13	5	5	41	42	146
0	0	6	210	235	90
0	2	6	53	54	0
0	4	6	184	193	-90
0	6	6	248	266	0
0	8	6	166	166	-90
0	10	6	217	226	0
0	12	6	148	160	-90
0	14	6	0	12	180
0	16	6	113	126	-90
1	1	6	54	44	180
1	3	6	50	33	-90
1	5	6	31	34	180
1	7	6	0	13	-90
1	9	6	75	71	180
1	11	6	54	44	90
1	13	6	66	60	0
1	15	6	172	174	-90
2	0	6	107	102	0
2	2	6	40	29	0
2	4	6	122	121	113
2	6	6	177	165	11
2	8	6	173	178	91
2	10	6	175	176	-10
2	12	6	123	139	2
2	14	6	62	76	106
2	16	6	135	137	-135
3	1	6	131	138	-83
3	3	6	92	87	155
3	5	6	48	48	77
3	7	6	44	49	90
3	9	6	52	45	114
3	11	6	86	90	-138
3	13	6	55	20	-119
3	15	6	110	105	-93
3	17	6	125	121	73
4	0	6	129	149	169
4	2	6	51	37	127
4	4	6	163	126	154
4	6	6	152	155	-63
4	8	6	124	103	165
4	10	6	51	40	-104
4	12	6	45	47	30
4	14	6	37	35	41
4	16	6	51	52	102
5	1	6	64	54	45
5	3	6	51	52	61
5	5	6	108	114	180
5	7	6	73	74	-82
5	9	6	96	93	-147
5	11	6	137	106	-78
5	13	6	41	29	25
5	15	6	61	65	90
6	0	6	98	97	-90
6	2	6	37	24	0
6	4	6	60	76	131
6	6	6	51	25	104
6	8	6	36	37	24
6	10	6	57	57	-101
6	12	6	67	73	159
7	1	6	22	19	0
7	3	6	77	81	116
7	5	6	45	45	26
7	7	6	25	26	90
7	9	6	83	86	82
8	0	6	104	104	-149
8	2	6	140	112	-147
8	4	6	111	121	-138

H	K	L	FOBS	FCAL	PHASE
9	0	0	29	29	32
9	9	0	69	68	95
9	10	0	74	79	-11
9	11	0	71	69	134
9	12	0	49	50	28
10	0	0	94	69	180
10	1	0	73	75	19
10	2	0	62	57	-96
10	3	0	0	5	-15
10	4	0	82	81	53
10	5	0	62	61	123
10	6	0	135	129	-161
10	7	0	66	72	41
10	8	0	75	68	-144
10	9	0	112	109	20
10	10	0	19	22	-60
11	0	0	44	49	180
11	1	0	84	81	-2
11	2	0	47	42	59
11	3	0	19	17	-119
11	4	0	88	88	129
11	5	0	100	93	-166
11	6	0	124	122	-147
11	7	0	33	29	-67
11	8	0	93	101	136
12	0	0	53	47	180
12	1	0	41	39	8
12	2	0	27	20	-45
12	3	0	73	71	78
12	4	0	40	39	75
12	5	0	29	30	-140
0	1	7	112	101	-90
0	2	7	178	146	180
0	3	7	56	48	90
0	4	7	209	215	0
0	5	7	93	104	90
0	6	7	36	6	-180
0	7	7	102	105	-90
0	8	7	104	112	180
0	9	7	57	44	-90
0	10	7	31	22	180
0	11	7	77	68	90
0	12	7	184	171	0
0	13	7	101	87	90
0	14	7	16	8	0
0	15	7	0	3	90
0	16	7	55	46	180
1	0	7	150	157	-90
1	1	7	326	352	-155
1	2	7	120	131	-97
1	3	7	150	160	72
1	4	7	165	161	169
1	5	7	121	124	-132
1	6	7	88	91	-168
1	7	7	85	86	0
1	8	7	31	26	-35
1	9	7	72	61	-30
1	10	7	64	50	-42
1	11	7	86	65	-76
1	12	7	43	40	-163
1	13	7	93	90	122
1	14	7	16	19	-129
1	15	7	19	27	5
1	16	7	19	23	156
2	0	7	64	62	-90
2	1	7	49	44	-88
2	2	7	120	94	81
2	3	7	185	200	107
2	4	7	106	136	174
2	5	7	88	87	104
2	6	7	54	53	-75
2	7	7	147	153	-94
2	8	7	169	168	166
2	9	7	152	145	-37
2	10	7	33	19	130
2	11	7	60	56	-63
2	12	7	29	39	54
2	13	7	56	51	33
2	14	7	29	31	-9
2	15	7	36	39	86
3	0	7	54	53	90
3	1	7	120	145	139
3	2	7	132	126	22
3	3	7	74	63	173
3	4	7	167	172	-171
3	5	7	33	26	26
3	6	7	121	121	121
3	7	7	83	83	-32
3	8	7	52	56	176
3	9	7	142	139	-104
3	10	7	132	104	-167
3	11	7	60	57	-146
3	12	7	54	43	131
3	13	7	70	72	97
3	14	7	46	44	128
3	15	7	25	26	112
4	0	7	66	67	-90
4	1	7	92	91	11
4	2	7	91	84	102
4	3	7	104	102	142
4	4	7	123	127	-173
4	5	7	148	148	-104
4	6	7	197	202	173
4	7	7	114	107	11
4	8	7	81	78	63
4	9	7	33	30	-142
4	10	7	47	38	-176
4	11	7	29	22	74
4	12	7	59	56	159
4	13	7	56	55	69
4	14	7	41	34	-92
4	15	7	73	80	-118
5	0	7	36	20	90
5	1	7	96	96	35
5	2	7	75	68	150
5	3	7	73	70	32
5	4	7	128	131	-123
5	5	7	251	213	23
5	6	7	95	90	-65
5	7	7	182	180	-38
5	8	7	133	107	-129
5	9	7	111	112	-79
5	10	7	169	166	-26
5	11	7	38	38	-22
5	12	7	44	41	-115
5	13	7	117	112	-66
5	14	7	66	67	-46
6	0	7	35	20	90
6	1	7	132	136	40
6	2	7	43	42	129
6	3	7	43	29	18
6	4	7	123	118	-137
6	5	7	83	55	44
6	6	7	69	61	173
6	7	7	65	74	-68
6	8	7	48	45	1
6	9	7	55	51	153
6	10	7	22	22	54
6	11	7	62	60	146
6	12	7	29	22	153
6	13	7	54	56	148
7	0	7	123	120	90
7	1	7	115	109	126
7	2	7	77	75	26
7	3	7	84	86	60
7	4	7	83	53	57
7	5	7	25	14	170
7	6	7	122	124	-63
7	7	7	83	58	-178
7	8	7	22	19	179
7	9	7	22	16	134
7	10	7	64	62	130
7	11	7	106	105	-65
7	12	7	59	64	-16
8	0	7	99	104	-90
8	1	7	31	24	25
8	2	7	41	33	123
8	3	7	200	186	-33
8	4	7	22	22	-55
8	5	7	145	130	-31
8	6	7	60	71	-46
8	7	7	33	23	-174
8	8	7	55	50	34
8	9	7	52	53	28
8	10	7	37	32	7
8	11	7	93	104	94
9	0	7	84	85	90
9	1	7	106	102	-142
9	2	7	71	65	32
9	3	7	101	105	130
9	4	7	80	69	166
9	5	7	60	50	-52
9	6	7	53	52	-145
9	7	7	77	83	139
9	8	7	27	16	-173
9	9	7	37	33	137
10	0	7	63	60	-90
10	1	7	81	77	171
10	2	7	77	66	-4
10	3	7	68	62	-46
10	4	7	65	61	-106
10	5	7	79	76	-80
10	6	7	179	165	-64
11	0	7	68	73	-90
0	0	6	137	120	0
0	1	6	86	87	-90
0	2	6	201	212	0
0	3	6	0	0	90
0	4	6	234	227	0
0	5	6	135	128	-90
0	6	6	0	8	180
0	7	6	149	143	90
0	8	6	31	33	0
0	9	6	64	54	-90
0	10	6	47	46	-180
0	11	6	40	30	-90
0	12	6	47	44	180
0	13	6	71	69	-90
1	0	6	94	87	0
1	1	6	47	49	50
1	2	6	141	149	151
1	3	6	94	101	180
1	4	6	121	123	-19
1	5	6	88	90	-104
1	6	6	56	51	92
1	7	6	133	133	23
1	8	6	83	88	-98
1	9	6	122	119	-8
1	10	6	47	36	28
1	11	6	93	88	44
1	12	6	59	55	154
1	13	6	48	50	72
2	0	6	196	193	0
2	1	6	41	39	147
2	2	6	88	89	127
2	3	6	192	186	-5
2	4	6	89	94	-103
2	5	6	111	102	147
2	6	6	47	46	180
2	7	6	135	127	6
2	8	6	212	215	148
2	9	6	210	209	32
2	10	6	86	75	159
2	11	6	71	69	-148
2	12	6	51	48	-174
3	0	6	61	60	180
3	1	6	56	49	145
3	2	6	106	104	153
3	3	6	31	32	-76
3	4	6	84	86	137
3	5	6	106	102	88
3	6	6	62	57	-54
3	7	6	94	85	40
3	8	6	158	144	176
3	9	6	108	94	39
3	10	6	59	49	131
3	11	6	109	104	102
3	12	6	38	37	103
4	0	6	61	56	180
4	1	6	35	28	-58
4	2	6	116	108	160
4	3	6	0	7	177
4	4	6	85	89	-117
4	5	6	183	186	69
4	6	6	64	58	-13
4	7	6	40	33	121
4	8	6	114	136	88
4	9	6	77	71	88
4	10	6	97	89	160
4	11	6	94	97	84
4	12	6	33	39	-157
5	0	6	186	189	180
5	1	6	40	38	161
5	2	6	78	76	124
5	3	6	122	114	-63
5	4	6	94	87	-152
5	5	6	86	79	-5
5	6	6	0	2	-5
5	7	6	177	177	-89
5	8	6	37	35	-10
5	9	6	93	95	99
5	10	6	161	160	156
5	11	6	84	94	-117
6	0	6	60	54	180
6	1	6	129	123	-137
6	2	6	86	88	-18
6	3	6	110	111	125
6	4	6	80	69	-5
6	5	6	46	36	-36
6	6	6	65	62	-26
6	7	6	68	64	-177
6	8	6	62	55	89
6	9	6	46	40	-176
6	10	6	27	26	77
7	0	6	29	15	0
7	1	6	65	61	12
7	2	6	48	45	92
7	3	6	72	63	-52
7	4	6	55	42	104
7	5	6	65	63	18
7	6	6	81	75	8
7	7	6	46	43	61
7	8	6	40	37	-51
8	0	6	104	100	180
8	1	6	79	79	-176
8	2	6	38	27	73
8	3	6	113	114	34
8	4	6	129	126	11
8	5	6	47	48	151
8	6	6	29	22	102
9	0	6	69	69	0
9	1	6	84	73	36
9	2	6	103	116	-161
0	1	9	40	29	-90
0	2	9	27	8	0
0	3	9	49	50	-90
0	4	9	27	16	0
0	5	9	156	152	-90
0	6	9	84	83	180
0	7	9	40	38	90
0	8	9	38	43	180
0	9	9	40	50	90
1	0	9	33	29	-90
1	1	9	84	80	-166
1	2	9	43	38	-107
1	3	9	62	54	-6
1	4	9	74	66	-117
1	5	9	64	57	-37
1	6	9	78	76	-136
1	7	9	55	56	12
1	8	9	103	105	-90
1	9	9	46	54	-108
2	0	9	131	129	-90
2	1	9	129	132	-5
2	2	9	84	82	160
2	3	9	67	61	1
2	4	9	19	14	-32
2	5	9	79	75	-60
2	6	9	22	15	-68
2	7	9	141	137	-11
2	8	9	140	136	-136
3	0	9	78	74	90
3	1	9	19	16	93
3	2	9	59	57	70
3	3	9	62	60	151
3	4	9	54	53	72
3	5	9	85	83	99
3	6	9	53	46	-177
3	7	9	118	115	-71
4	0	9	76	75	-90
4	1	9	24	17	-112
4	2	9	0	5	-113
4	3	9	33	33	163
4	4	9	43	39	99
4	5	9	35	31	-155
4	6	9	88	87	7
4	7	9	81	93	-145
5	0	9	52	49	90
5	1	9	29	22	3
5	2	9	84	80	-43
5	3	9	37	32	63
5	4	9	47	41	135
5	5	9	37	31	-112
6	0	9	11	4	-90
6	1	9	36	30	132
6	2	9	48	58	176
6	3	9	55	60	90

APPENDIX V

Diethylidene Trehalose: Table of Normalised Structure Factors and Phases.

h	k	ℓ	E_K	E_W	φ_S	φ_F	h	k	ℓ	E_K	E_W	φ_S	φ_F
-1	0	5	4.60	4.97	0°	0°	11	6	2	2.29	2.24	85°	133°
-13	1	6	4.06	4.00	177	177	7	5	0	2.29	2.55	89	132
4	1	7	3.32	3.71	4	46	6	0	7	2.28	2.53	0	0
-12	0	6	3.30	3.40	180	180	-5	3	6	2.26	2.52	87	47
3	7	0	3.26	3.65	-178	-147	4	10	1	2.26	2.22	-6	-1
-3	0	6	3.25	3.57	180	180	8	3	0	2.24	2.50	-77	-61
-11	2	6	3.22	3.40	-4	-3	-2	1	5	2.24	2.43	12	-2
3	8	1	3.15	3.45	-179	-140	3	0	7	2.23	2.49	0	0
6	0	2	3.14	3.42	0	0	12	5	2	2.23	2.16	85	70
5	0	7	3.11	3.48	0	0	-9	1	8	2.22	2.37	170	-158
-6	0	8	3.01	3.36	180	180	2	3	8	2.22	2.48	94	107
-13	0	5	2.97	3.00	180	180	-4	3	7	2.21	2.57	-169	-114
10	0	7	2.96	2.97	180		-5	3	12	2.18	2.10		
-9	0	9	2.92	3.06	0	0	3	4	9	2.18	2.31	90	105
-7	0	7	2.89	3.23	180	180	3	1	7	2.17	2.42	0	-28
4	2	7	2.83	3.16	178	132	3	1	3	2.16	2.30	-96	-91
2	10	1	2.77	2.80	-2	14	5	5	5	2.15	2.40	89	10
-3	4	7	2.73	3.05	91	48	-11	1	7	2.13	2.23	176	91
-5	1	8	2.72	3.04	168	-127	-9	0	1	2.13	2.37	180	180
6	5	0	2.68	2.99	88	46	-10	0	1	2.13	2.37	180	0
5	10	0	2.56	2.49	-115	-43	-5	0	7	2.10	2.34		
-4	2	7	2.54	2.83	-83	-80	-10	0	6	2.10	2.28	180	180
13	0	4	2.51	2.42	0	0	-2	4	2	2.09	2.27	93	40
-6	0	12	2.51	2.45			-7	5	5	2.09	2.31	-92	-97
2	8	1	2.47	2.72	177	138	-1	1	6	2.08	2.27	-3	62
4	0	7	2.46	2.74	0	180	5	2	2	2.07	2.26	173	146
6	6	7	2.45	2.50	3	67	8	2	1	2.02	2.25	81	71
3	1	12	2.42	2.33	-2	37	-9	0	8	2.01	2.16	0	0
1	0	4	2.42	2.56	180	180	2	1	8	1.99	2.23	-76	-120
-10	2	1	2.40	2.68	5	-38	-13	0	6	1.99	1.96	180	180
-11	3	7	2.39	2.43	-12	57	3	10	1	1.98	1.97	12	-115
10	2	0	2.38	2.65	-94	-117	-4	5	6	1.98	2.22	-90	173
-11	0	1	2.37	2.61	180	180	-1	5	7	1.98	2.20	-95	-77
14	0	1	2.36	2.29	180	0	1	2	0	1.97	2.04	172	156
3	0	12	2.36	2.28	0	180	5	1	2	1.97	2.13	6	74
4	0	8	2.36	2.63	180	180	-4	3	1	1.96	2.11	88	77
-10	1	6	2.35	2.55	57	69	-5	4	7	1.96	2.18	94	130
4	0	2	2.33	2.48	0	0	7	5	7	1.95	2.00	-42	99
-2	1	6	2.33	2.55	-15	-80	8	7	3	1.95	2.01	-2	-46
-6	1	8	2.32	2.59	167	105	2	7	1	1.95	2.17	3	-44

h	k	ℓ	E_K	E_W	φ_S	φ_F	h	k	ℓ	E_K	E_W	φ_S	φ_F
6	1	1	1.94	2.12	178°	177°	-9	1	1	1.71	1.92		
-1	0	3	1.94	2.01			-8	0	11	1.71	1.70	0°	180°
-6	1	7	1.92	2.15	27	21	-13	0	1	1.71	1.77		
-12	1	6	1.92	1.97	159	128	9	2	0	1.71	1.91	-94	-12
-5	0	9	1.92	2.12	0	0	-7	3	10	1.70	1.74	99	-33
0	5	8	1.92	2.09	-92	-169	8	5	1	1.69	1.88	72	167
3	3	8	1.91	2.11	99	60	5	5	9	1.69	1.70	-94	-58
9	0	4	1.90	2.11	180	0	8	4	0	1.69	1.89	89	48
3	8	5	1.90	2.00	-53	-99	-2	1	4	1.67	1.78	-169	68
-2	2	6	1.89	2.08	44	14	-1	3	6	1.67	1.84	153	53
-2	5	7	1.88	2.10	-91	17	2	8	0	1.66	1.83	173	172
5	1	6	1.87	2.09	179	177	-12	6	1	1.66	1.59	163	-178
-4	3	6	1.87	2.08	98	161	2	0	10	1.65	1.78	180	180
-13	4	2	1.87	1.83			6	5	8	1.65	1.69	-178	164
-6	6	1	1.87	2.09	-93	-59	-13	4	4	1.65	1.60	91	103
7	6	7	1.86	1.84	10	-68	11	4	1	1.65	1.75	92	173
7	6	0	1.86	2.06	-89	152	0	2	4	1.65	1.76	73	33
-7	1	8	1.86	2.05	-179	162	7	5	4	1.65	1.80	-88	-157
-1	3	2	1.84	1.95	86	74	1	2	8	1.64	1.83	-71	-63
4	1	6	1.84	2.05	-170	78	1	6	1	1.64	1.81	45	79
4	5	9	1.83	1.88	-86	-44	7	0	2	1.64	1.80	0	0
9	1	1	1.83	2.05	95	110	4	6	1	1.64	1.82	19	-4
-2	0	9	1.83	2.05	180	180	-6	2	8	1.64	1.81	18	88
-9	6	6	1.82	1.86	-107	-133	7	7	0	1.63	1.76	-92	-167
13	1	3	1.81	1.78	-177	159	-6	0	9	1.63	1.79	0	180
-8	1	8	1.80	1.96	175	172	4	1	8	1.63	1.81	-32	-72
7	5	6	1.79	1.90	80	-161	2	9	2	1.63	1.72	-168	-164
-6	2	7	1.79	2.00	-50	-7	3	9	5	1.63	1.62	2	-26
7	6	6	1.79	1.83	114	-11	2	2	12	1.62	1.57	166	33
12	0	4	1.79	1.81	0	0	-1	4	2	1.62	1.75	87	-62
-11	2	8	1.79	1.79	160	-152	4	9	0	1.61	1.70	-5	-12
-9	1	7	1.78	1.95	176	-140	8	2	5	1.61	1.78	-110	27
12	4	0	1.77	1.81	81	78	0	9	2	1.61	1.71	115	110
1	7	1	1.77	1.98	-6	27	-11	0	6	1.61	1.71	180	0
3	7	5	1.77	1.92	178	154	6	6	8	1.60	1.58		
5	1	7	1.76	1.97	-12	-62	-10	4	6	1.60	1.69	131	179
5	5	1	1.75	1.95	-75	-31	6	6	3	1.60	1.77	123	94
-11	0	5	1.75	1.89			-7	4	7	1.59	1.74	46	19
-12	4	5	1.75	1.75	81	53	1	0	9	1.59	1.78		
8	2	9	1.75	1.72	68	62	-1	4	7	1.59	1.78		
8	4	6	1.75	1.86	-87	-109	4	5	8	1.59	1.69	-120	-98
-3	3	12	1.75	1.71	76	133	6	3	5	1.59	1.77	-87	-147
8	6	6	1.74	1.74	135	-117	8	3	1	1.58	1.77	-84	-127
12	5	1	1.74	1.72	87	136	-2	1	1	1.58	1.62	-48	-27
-8	5	1	1.74	1.94	96	22	-7	6	6	1.58	1.69	-93	-67
-2	3	7	1.74	1.94	87	100	-1	2	1	1.58	1.63	71	29
-5	2	12	1.73	1.70	-73	-69	-11	2	2	1.58	1.73	-154	1
3	6	6	1.73	1.90	3	-23	1	6	8	1.57	1.67	-108	-75
-2	0	1	1.73	1.76	180	180	6	0	1	1.57	1.72	0	180
-4	4	6	1.73	1.93			0	1	1	1.57	1.59	-3	43

h	k	ℓ	E_K	E_W	φ_S	φ_F	h	k	ℓ	E_K	E_W	φ_S	φ_F
-2	1	3	1.57	1.64	51°	32°	6	4	0	1.45	1.61		
8	6	2	1.56	1.69	14	-82	-2	6	7	1.45	1.59	-95°	-105°
-2	4	6	1.56	1.74	-87	1	5	1	1	1.45	1.56	178	103
-5	2	7	1.56	1.75	-70	-142	6	2	1	1.45	1.58	119	-164
2	0	1	1.56	1.59	0	180	6	0	6	1.44	1.61	180	0
2	5	8	1.56	1.69	-87	136	-5	3	8	1.44	1.60	-52	-97
5	5	8	1.56	1.62	-154	-112	5	2	6	1.44	1.61	103	-173
-1	4	8	1.55	1.73	87	101	-1	4	1	1.44	1.55	-85	-64
10	1	0	1.55	1.74	178	108	10	3	1	1.43	1.58	-90	-89
-12	1	7	1.54	1.55	168	-152	-5	4	1	1.43	1.58	87	-146
6	2	5	1.54	1.72			-10	1	7	1.42	1.52	174	-49
1	3	8	1.54	1.72	89	30	-6	5	4	1.42	1.59	122	153
9	7	2	1.54	1.56	172	-143	0	1	5	1.42	1.54		
8	2	0	1.53	1.71	-96	168	0	2	5	1.41	1.54	180	133
-3	3	6	1.53	1.70	104	44	1	8	1	1.41	1.56	179	-159
2	0	11	1.53	1.59	0	180	5	6	1	1.40	1.57	47	53
8	0	5	1.53	1.70	0	0	2	5	0	1.40	1.54	-18	33
7	2	6	1.52	1.69	84	93	-9	1	6	1.40	1.56	50	-138
0	3	9	1.52	1.67	-92	-83	8	2	2	1.40	1.57	158	159
-12	0	1	1.52	1.63	180	180	-3	6	3	1.40	1.56	140	83
-3	3	7	1.52	1.70	95	168	7	1	1	1.39	1.54	178	-150
8	5	2	1.52	1.67	-22	103	-9	3	5	1.39	1.54	99	136
-9	6	7	1.51	1.50	163	167	-1	5	1	1.39	1.52	-111	-179
6	6	5	1.51	1.62	-80	145	-4	5	1	1.38	1.53	-89	2
1	6	2	1.51	1.67	122	97	2	2	9	1.38	1.52	-81	-67
2	2	0	1.51	1.57	147	153	-6	3	7	1.38	1.55	-102	-27
-1	6	2	1.50	1.66	-95	-135	-7	4	6	1.38	1.54	91	48
6	8	1	1.50	1.59			0	2	9	1.37	1.53	-50	-27
8	1	6	1.50	1.63	93	116	3	7	1	1.37	1.53		
-2	2	5	1.50	1.63	-178	158	7	4	1	1.37	1.53	-84	-103
6	7	4	1.49	1.58	138	69	1	6	6	1.36	1.50	14	96
-4	1	7	1.49	1.65	-31	-36	9	4	0	1.36	1.50	93	11
9	4	1	1.49	1.64	-83	-120	-4	3	8	1.35	1.52	-85	-98
7	1	2	1.48	1.63	-152	-117	-9	2	4	1.35	1.52	67	42
-10	2	5	1.48	1.61	-97	-67	5	6	0	1.35	1.50	104	151
6	7	0	1.46	1.60	-104	-28	9	3	1	1.35	1.50	-84	-17
5	8	0	1.46	1.57	15	18	9	2	1	1.34	1.50	87	39
5	2	1	1.46	1.58	155	25	-7	0	4		1.82	0	180
3	0	8	1.46	1.63	180	180	2	3	7		1.60	160	134
-1	5	2	1.46	1.60	-95	-27	0	0	4	2.28	2.42	180	0
3	9	1	1.46	1.54			0	0	7	2.00	2.20	180	180
-3	5	6	1.46	1.63	-96	-67	4	0	0	1.97	2.06		
-3	5	1	1.45	1.60	-95	-173	0	0	6	1.87	2.04		
1	7	2	1.45	1.62	34	57	9	0	0	1.75	1.95		

E_K = value obtained from K-curve; E_W from Wilson plot.

φ_S = value from Σ_2 refinement; φ_F = final refined value.

APPENDIX VI

Diethylidene Trehalose Structure Factor Data.

(Scale is ten times absolute.)

k	ℓ	h	F_o	F_c	φ	h	F_o	F_c	φ	h	F_o	F_c	φ	h	F_o	F_c	φ
0	0	1	23	36	-180°	2	225	221	0°	3	80	52	0°	4	582	619	0°
		5	180	127	-180	6	133	124	-180	7	42	41	-180	8	170	178	-180
		9	209	210	0	10	37	37	-180	11	40	38	-180	12	78	68	-180
		13	0	16	-180	14	41	32	0								
0	1	-14	55	61	0	-13	96	88	-180	-12	105	103	-180	-11	199	188	-180
		-10	216	222	0	-9	260	280	-180	-8	57	56	0	-7	107	106	0
		-6	118	108	0	-5	189	175	-180	-4	403	402	0	-3	368	406	-180
		-2	664	963	-180	-1	78	65	0	0	464	489	0	1	37	8	0
		2	582	650	-180	3	265	203	-180	4	202	191	0	5	317	270	0
		6	317	296	-180	7	39	45	-180	8	25	3	0	9	60	61	-180
		10	0	13	0	11	57	58	-180	12	33	22	-180	13	23	12	0
		14	99	88	0												
0	2	-14	56	49	0	-13	0	43	-180	-12	49	62	-180	-11	45	41	0
		-10	70	63	0	-9	142	143	-180	-8	80	62	-180	-7	0	10	0
		-6	109	112	0	-5	229	225	-180	-4	131	141	-180	-3	145	145	0
		-2	0	3	-180	-1	143	120	-180	0	518	434	0	1	27	15	0
		2	25	16	-180	3	83	39	0	4	597	574	0	5	0	19	0
		6	576	625	0	7	251	246	0	8	134	134	0	9	63	69	0
		10	0	10	0	11	56	59	-180	12	58	50	-180	13	34	30	0
0	3	-14	23	13	0	-13	0	20	-180	-12	40	39	-180	-11	76	58	-180
		-10	94	103	0	-9	68	80	-180	-8	86	92	0	-7	0	23	0
		-6	97	98	0	-5	63	101	-180	-4	21	12	-180	-3	102	118	-180
		-2	58	85	-180	-1	626	505	0	0	50	24	-180	1	48	41	-180
		2	201	123	0	3	91	67	-180	4	263	205	-180	5	112	108	-180
		6	85	72	0	7	47	34	-180	8	27	10	-180	9	27	36	-180
		10	0	1	-180	11	27	17	0	12	0	15	0	13	0	5	0
0	4	-14	0	17	0	-13	23	18	-180	-12	0	12	-180	-11	61	56	-180
		-10	31	46	-180	-9	0	7	0	-8	59	68	-180	-7	246	249	-180
		-6	85	75	-180	-5	117	119	0	-4	45	18	-180	-3	319	293	-180
		-2	0	32	0	-1	137	131	0	0	620	509	0	1	630	518	-180
		2	21	21	0	3	0	7	-180	4	166	123	0	5	57	42	0
		6	111	89	0	7	74	64	0	8	37	44	-180	9	168	175	0
		10	78	76	-180	11	0	11	0	12	89	75	0	13	101	100	0
0	5	-14	42	39	-180	-13	148	109	-180	-12	54	45	-180	-11	127	125	-180
		-10	110	109	0	-9	85	104	-180	-8	33	43	0	-7	157	161	-180
		-6	105	103	-180	-5	139	139	0	-4	89	83	0	-3	244	205	-180
		-2	79	95	-180	-1	1053	970	0	0	168	125	0	1	86	54	0
		2	25	4	-180	3	132	104	0	4	71	59	-180	5	193	174	0
		6	93	85	-180	7	120	115	-180	8	143	134	0	9	61	51	0
		10	92	87	-180	11	40	52	-180	12	42	36	0				
0	6	-13	90	76	-180	-12	180	135	-180	-11	105	83	0	-10	162	145	-180
		-9	0	6	0	-8	77	74	0	-7	62	54	-180	-6	29	20	-180
		-5	119	101	0	-4	175	156	-180	-3	562	460	-180	-2	72	37	-180
		-1	177	133	-180	0	338	249	-180	1	132	106	-180	2	0	20	-180
		3	0	15	0	4	154	128	0	5	0	12	0	6	154	161	0
		7	0	22	-180	8	0	10	-180	9	0	45	0	10	0	29	-180

k	ℓ	h	F_o	F_c	φ	h	F_o	F_c	φ	h	F_o	F_c	φ	h	F_o	F_c	φ
0	7	-13	63	39	0	-12	68	55	0	-11	0	22	0	-10	71	60	-180
		-9	0	37	-180	-8	0	9	-180	-7	302	258	-180	-6	55	52	-180
		-5	267	231	-180	-4	94	82	0	-3	142	87	-180	-2	0	3	0
		-1	205	187	0	0	298	214	-180	1	117	87	0	2	0	8	-180
		3	282	247	0	4	283	274	-180	5	322	313	0	6	208	202	0
		7	104	95	0	8	0	13	-180	9	0	20	0				
0	8	-11	0	16	-180	-10	0	10	-180	-9	143	115	0	-8	0	16	0
		-7	0	29	-180	-6	299	280	-180	-5	112	99	0	-4	78	65	-180
		-3	55	40	-180	-2	63	52	-180	-1	165	147	0	0	71	73	-180
		1	0	14	0	2	0	13	-180	3	152	142	-180	4	226	196	-180
		5	64	62	-180	6	0	16	-180	7	0	21	0	8	0	47	-180
		9	21	22	-180												
0	9	-11	25	10	-180	-10	0	3	0	-9	176	124	0	-8	0	18	0
		-7	0	1	-180	-6	135	105	-180	-5	171	146	0	-4	46	36	-180
		-3	108	105	-180	-2	184	159	-180	-1	46	38	-180	0	56	41	-180
		1	152	137	-180	2	56	57	-180	3	46	23	0	4	0	34	0
		5	52	58	0	6	0	5	-180	7	48	54	0				
0	10	-9	45	53	0	-8	74	52	-180	-7	50	37	-180	-6	0	26	-180
		-5	0	37	0	-4	33	5	-180	-3	66	45	-180	-2	80	63	0
		-1	0	7	-180	0	33	22	0	1	0	29	-180	2	127	114	-180
		3	0	8	0	4	40	45	0	5	0	9	0	6	68	78	-180
		7	61	56	0												
0	11	-9	33	29	0	-8	86	60	-180	-7	0	18	-180	-6	53	42	0
		-5	48	47	-180	-4	58	47	-180	-3	42	24	0	-2	53	42	-180
		-1	0	20	-180	0	42	49	-180	1	58	44	0	2	96	89	-180
		3	52	51	0	4	65	55	-180	5	60	54	0				
0	12	-7	39	32	-180	-6	117	94	-180	-5	57	54	0	-4	58	60	-180
		-3	50	59	0	-2	0	16	-180	-1	0	19	-180	0	0	44	-180
		1	0	11	0	2	0	0	0	3	106	110	-180				
1	0	1	316	347	149	2	491	557	-134	3	286	276	-175	4	329	306	-63
		5	33	9	135	6	109	98	94	7	78	71	-179	8	151	150	4
		9	119	120	-169	10	152	166	108	11	88	81	-166	12	0	15	81
		13	61	57	-130	14	23	9	-79								
1	1	-14	0	18	-140	-13	39	39	112	-12	71	72	152	-11	0	8	-120
		-10	99	98	-44	-9	207	237	61	-8	60	58	165	-7	77	74	-82
		-6	175	171	-43	-5	58	72	-70	-4	169	170	112	-3	354	388	-100
		-2	587	889	-27	-1	441	464	-54	0	633	839	43	1	129	179	-40
		2	279	254	-62	3	231	180	-145	4	154	134	108	5	341	350	103
		6	384	398	177	7	229	241	-150	8	132	141	163	9	210	215	110
		10	62	60	120	11	36	19	-151	12	44	45	1	13	36	38	-123
		14	31	26	54												
1	2	-14	0	4	38	-13	39	33	-136	-12	27	38	127	-11	92	94	-130
		-10	72	82	63	-9	99	112	-44	-8	76	71	140	-7	69	58	-103
		-6	149	167	-23	-5	247	263	15	-4	65	72	154	-3	102	108	-74
		-2	462	436	-52	-1	268	202	93	0	39	47	-162	1	307	325	142
		2	127	93	13	3	251	269	-93	4	341	318	25	5	421	401	74
		6	173	171	-56	7	224	240	-117	8	34	27	-122	9	114	121	139
		10	29	25	-139	11	80	81	-118	12	39	33	4	13	33	29	161
1	3	-14	23	26	-171	-13	39	31	-87	-12	37	30	73	-11	49	52	99
		-10	83	89	-37	-9	57	72	7	-8	47	50	-32	-7	141	145	137
		-6	151	154	-40	-5	166	180	102	-4	285	306	-82	-3	128	134	134
		-2	469	420	32	-1	212	197	-53	0	129	92	-83	1	193	165	-165
		2	282	272	61	3	541	488	-91	4	142	118	20	5	71	52	-42

k	ℓ	h	F_o	F_c	φ	h	F_o	F_c	φ	h	F_o	F_c	φ	h	F_o	F_c	φ
1	3	6	178	180	49	7	137	127	-98	8	0	23	19	9	79	69	142
		10	87	90	102	11	48	48	-156	12	34	32	-160	13	80	70	159
1	4	-14	47	30	-138	-13	29	33	150	-12	0	24	43	-11	40	32	-96
		-10	93	103	-78	-9	0	34	-44	-8	55	52	-26	-7	69	68	-52
		-6	103	104	17	-5	89	92	-63	-4	36	44	61	-3	228	214	-114
		-2	430	374	68	-1	292	244	-100	0	119	89	138	1	314	290	-164
		2	280	267	51	3	77	65	-95	4	231	206	-60	5	183	164	127
		6	65	70	33	7	75	65	-179	8	105	102	-100	9	78	72	147
		10	60	57	39	11	31	19	30	12	41	45	-43	13	42	39	-110
1	5	-14	21	21	-127	-13	27	26	164	-12	85	94	54	-11	55	57	-44
		-10	89	87	-5	-9	99	103	145	-8	0	25	96	-7	97	109	-123
		-6	64	72	25	-5	78	78	89	-4	197	181	20	-3	188	158	-47
		-2	490	443	-2	-1	263	188	5	0	315	260	34	1	255	236	-139
		2	253	212	-47	3	90	83	-34	4	124	112	22	5	63	44	117
		6	53	53	-55	7	70	68	-1	8	53	44	-164	9	58	60	102
		10	27	22	26	11	23	14	-4	12	29	24	-84				
1	6	-13	182	144	177	-12	105	85	128	-11	53	44	-149	-10	180	175	69
		-9	125	114	-138	-8	72	51	103	-7	71	54	-82	-6	62	54	-34
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		7	45	46	14	8	45	43	172	9	25	24	-129	10	36	35	-82
		11	23	21	118	12	18	19	-175								
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		-8	61	64	53	-7	116	147	29	-6	76	72	-138	-5	168	172	-155
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		0	81	63	114	1	34	23	132	2	56	53	-109	3	50	37	-85
		4	92	92	-88	5	88	81	9	6	112	129	-108	7	79	77	5
		8	83	89	-8	9	40	38	-179	10	0	12	-166				
4	6	-12	23	20	-9	-11	34	28	-18	-10	104	94	179	-9	100	95	171
		-8	100	105	104	-7	133	133	48	-6	124	122	135	-5	143	159	158
		-4	217	232	151	-3	151	146	-7	-2	214	217	1	-1	187	199	-133
		0	0	13	85	1	69	69	38	2	74	66	-39	3	44	56	114
		4	45	44	-43	5	88	105	158	6	101	114	-122	7	75	75	13
		8	117	128	-109	9	53	50	129	10	27	26	178				
4	7	-11	46	48	-147	-10	31	28	87	-9	46	39	-119	-8	62	59	-30
		-7	136	143	19	-6	100	94	21	-5	201	212	130	-4	76	68	170
		-3	313	333	48	-2	123	121	-34	-1	189	196	113	0	98	111	-147
		1	68	61	-95	2	88	92	-68	3	23	25	-177	4	83	95	-158
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		9	29	23	27												

k	ℓ	h	F_o	F_c	φ	h	F_o	F_c	φ	h	F_o	F_c	φ	h	F_o	F_c	φ
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		-7	37	31	37	-6	55	61	-177	-5	69	63	-169	-4	107	115	169
		-3	70	71	-35	-2	62	65	150	-1	156	161	101	0	134	152	137
		1	87	92	-28	2	81	83	94	3	64	64	126	4	63	61	-18
		5	79	99	-60	6	71	68	-45	7	0	15	95	8	44	49	-96
4	9	-10	25	22	-175	-9	69	65	-37	-8	46	44	110	-7	62	56	135
		-6	36	43	-157	-5	64	68	90	-4	0	17	-2	-3	49	46	27
		-2	68	75	-83	-1	107	122	82	0	39	39	-29	1	55	57	72
		2	31	34	-158	3	154	176	105	4	45	40	15	5	36	38	14
		6	15	18	-106	7	54	55	168								
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		-4	0	29	97	-3	0	24	14	-2	23	28	-24	-1	29	28	177
		0	36	41	94	1	36	38	-96	2	48	56	-170	3	45	47	164
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		5	0	16	-114	6	331	365	46	7	248	247	132	8	66	70	139
		9	31	21	138	10	73	78	16	11	58	57	79	12	25	18	-68
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		-8	167	154	22	-7	135	125	-83	-6	117	106	-170	-5	85	70	-152
		-4	215	200	2	-3	246	226	-173	-2	192	169	-72	-1	260	209	-179
		0	161	165	119	1	202	208	147	2	56	69	25	3	36	28	163
		4	114	112	180	5	239	249	-31	6	115	120	7	7	139	145	-9
		8	155	166	167	9	85	84	1	10	44	31	39	11	70	70	100
		12	80	63	136												
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		-8	63	61	-62	-7	72	65	-155	-6	136	121	157	-5	65	67	-15
		-4	34	21	8	-3	188	163	-76	-2	179	161	-94	-1	256	216	-27
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		4	77	81	144	5	49	40	-107	6	82	87	24	7	55	47	178
		8	130	135	103	9	50	41	-105	10	27	22	51	11	31	26	135
		12	95	83	70												
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		-8	96	93	-37	-7	66	81	-152	-6	92	79	124	-5	52	29	-136
		-4	155	135	-25	-3	119	89	-134	-2	212	176	94	-1	114	96	14
		0	18	15	178	1	36	43	-150	2	111	118	145	3	0	14	-144
		4	31	39	149	5	102	109	-84	6	84	86	148	7	77	76	139
		8	74	69	75	9	21	24	-68	10	21	17	142	11	49	46	-35
5	4	-12	46	44	-104	-11	18	32	-137	-10	54	52	166	-9	0	27	-39
		-8	23	22	-112	-7	59	77	-119	-6	153	145	153	-5	58	32	-70
		-4	34	25	-92	-3	170	136	-64	-2	79	75	-144	-1	114	113	-102
		0	63	54	-44	1	147	144	-56	2	84	80	77	3	126	136	-158
		4	109	122	-13	5	126	147	-57	6	58	68	103	7	137	141	-157
		8	45	48	-26	9	25	26	-97	10	33	41	158				
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		-7	188	200	-97	-6	50	42	-4	-5	88	89	-63	-4	122	115	46
		-3	113	122	-92	-2	82	91	-5	-1	151	152	-175	0	59	50	144
		1	128	126	-13	2	39	36	-113	3	122	124	165	4	64	62	-24
		5	205	222	10	6	102	107	132	7	27	27	112	8	37	39	118
		9	68	63	-5	10	47	39	129								

k	ℓ	h	F_o	F_c	φ	h	F_o	F_c	φ	h	F_o	F_c	φ	h	F_o	F_c	φ
5	6	-11	0	22	138	-10	40	56	78	-9	60	82	48	-8	65	81	163
		-7	87	108	168	-6	55	57	-167	-5	68	72	-36	-4	204	223	173
		-3	158	170	-67	-2	31	38	-160	-1	77	88	-172	0	126	137	174
		1	72	59	-61	2	31	34	-156	3	87	93	-173	4	116	108	-64
		5	85	75	-60	6	79	76	-53	7	116	98	-161	8	80	62	51
		9	50	34	-88	10	37	30	108								
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		-3	83	89	-97	-2	184	205	17	-1	194	207	-77	0	112	120	-82
		1	120	121	-90	2	101	100	18	3	33	30	153	4	0	16	-150
		5	54	45	-49	6	76	65	-176	7	109	85	99	8	66	41	1
		9	47	29	-32												
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		-6	21	35	51	-5	67	73	-61	-4	23	37	-150	-3	106	119	103
		-2	101	112	92	-1	40	46	-166	0	159	156	-169	1	98	80	-75
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		6	89	73	164	7	56	33	119								
5	9	-9	15	28	-22	-8	71	71	81	-7	29	26	110	-6	18	22	131
		-5	27	31	-13	-4	21	17	-49	-3	61	61	14	-2	42	43	129
		-1	31	24	170	0	57	60	-76	1	36	29	42	2	61	55	60
		3	61	62	-49	4	101	97	-44	5	84	69	-58	6	64	51	-75
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		1	18	15	-139	2	0	9	146	3	21	30	152	4	34	30	23
5	11	-5	34	50	167	-4	42	44	-26	-3	31	29	141	-2	25	24	123
		-1	21	25	-179	0	23	23	-12	1	39	33	134				
6	0	0	75	64	-6	1	76	76	-18	2	131	141	-146	3	117	128	66
		4	37	31	-70	5	153	146	151	6	62	58	116	7	167	167	152
		8	29	22	-102	9	27	17	-173	10	39	39	-71	11	0	4	154
		12	18	25	119												
6	1	-12	68	68	-178	-11	56	49	34	-10	33	31	-32	-9	36	35	-142
		-8	86	88	-119	-7	98	93	76	-6	192	177	-59	-5	114	116	-114
		-4	120	114	-25	-3	159	154	112	-2	76	82	0	-1	27	32	68
		0	95	88	60	1	237	234	79	2	186	192	62	3	152	154	-26
		4	199	191	-4	5	156	164	53	6	103	93	125	7	46	41	93
		8	82	85	-12	9	37	44	-102	10	21	8	-49	11	33	27	57
6	2	-12	63	50	-85	-11	15	19	22	-10	36	29	-52	-9	63	60	-134
		-8	73	67	169	-7	31	38	75	-6	76	78	35	-5	65	53	-112
		-4	108	88	-149	-3	95	83	73	-2	105	106	47	-1	208	185	-135
		0	137	130	-158	1	206	202	97	2	108	110	131	3	86	80	-41
		4	101	98	-73	5	62	57	50	6	53	58	152	7	64	58	40
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6	3	-11	0	18	-73	-10	0	17	72	-9	29	42	-88	-8	81	71	-126
		-7	42	20	-19	-6	41	32	59	-5	44	34	147	-4	133	133	-95
		-3	168	146	83	-2	87	78	-1	-1	127	114	156	0	157	149	-95
		1	79	75	80	2	71	68	8	3	57	38	129	4	46	34	-36
		5	44	44	74	6	138	143	94	7	82	90	82	8	60	47	36
		9	55	55	-26	10	61	57	39	11	55	54	38				

k	l	h	F_o	F_c	φ	h	F_o	F_c	φ	h	F_o	F_c	φ	h	F_o	F_c	φ
6	4	-10	0	16	-101	-9	34	31	66	-8	58	42	-101	-7	67	64	150
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		-2	40	34	40	-1	39	32	92	0	63	56	84	1	79	75	-10
		2	73	70	126	3	60	59	-31	4	0	23	-146	5	71	79	-97
		6	49	49	129	7	54	49	173	8	0	5	-122	9	23	29	-34
		10	27	28	-17												
6	5	-10	27	32	-149	-9	27	21	-116	-8	54	63	-152	-7	37	26	59
		-6	31	47	-125	-5	68	64	-143	-4	37	45	55	-3	71	84	-154
		-2	78	86	-60	-1	63	51	-102	0	29	26	51	1	48	49	152
		2	76	82	39	3	44	35	-49	4	70	71	104	5	95	94	89
		6	109	102	145	7	21	14	-178	8	18	19	8	9	21	21	-5
6	6	-10	37	40	-154	-9	97	100	-133	-8	18	17	-18	-7	107	133	-67
		-6	63	63	-88	-5	88	91	-61	-4	85	91	133	-3	31	18	-56
		-2	52	48	39	-1	50	60	-159	0	78	84	116	1	123	127	96
		2	110	112	-33	3	141	131	-23	4	41	50	-24	5	74	69	82
		6	50	49	91	7	98	80	-11	8	83	70	-117	9	33	31	23
6	7	-10	23	26	163	-9	73	70	167	-8	25	28	-153	-7	0	16	-17
		-6	63	64	-179	-5	29	33	-160	-4	37	39	-139	-3	42	51	20
		-2	118	130	-105	-1	31	30	-153	0	21	38	180	1	98	106	174
		2	80	80	-13	3	36	32	-79	4	67	61	-139	5	37	36	-172
		6	132	129	67	7	89	75	-68								
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		-5	53	61	-113	-4	57	63	78	-3	90	110	-95	-2	72	76	-177
		-1	78	92	-53	0	29	29	179	1	107	110	-75	2	67	64	91
		3	18	16	-27	4	54	48	162	5	68	57	140	6	74	78	75
6	9	-8	34	44	45	-7	25	27	-56	-6	56	62	-98	-5	40	45	-59
		-4	39	46	-5	-3	40	52	-164	-2	72	79	-178	-1	18	20	51
		0	0	7	-50	1	18	22	-156	2	23	25	-103	3	23	23	-14
		4	42	52	-91	5	49	51	-115								
6	10	-5	34	32	-24	-4	42	43	81	-3	15	16	-120	-2	21	30	-173
		-1	57	63	-87	0	33	37	100	1	39	35	-107	2	25	26	133
7	0	1	105	100	66	2	106	107	-20	3	339	354	-147	4	117	104	174
		5	89	80	-146	6	119	112	-28	7	118	117	-167	8	0	42	-96
		9	0	19	-121	10	0	15	-62								
7	1	1	198	197	27	2	211	193	-44	3	140	135	-147	4	83	82	142
		5	87	83	107	6	0	15	41	7	0	12	-159	8	78	79	176
		9	0	22	9	10	33	30	-8								
7	2	0	103	96	100	1	154	159	57	2	84	60	-9	3	88	84	4
		4	40	37	103	5	55	42	118	6	80	75	-40	7	79	80	-133
		8	23	26	-134	9	78	65	-143	10	36	32	-160				
7	3	0	63	55	-69	1	40	34	126	2	74	72	-92	3	27	17	107
		4	0	19	-121	5	0	23	82	6	25	29	-64	7	0	13	100
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		4	41	48	13	5	27	26	-2	6	95	94	69	7	76	68	160
		8	71	69	-25	9	46	35	31								
7	5	0	42	37	59	1	90	87	2	2	94	106	-131	3	134	126	154
		4	70	70	-145	5	27	37	-18	6	36	37	-156	7	31	36	-153
		8	58	53	-104												

k	ℓ	h	F_o	F_c	φ	h	F_o	F_c	φ	h	F_o	F_c	φ	h	F_o	F_c	φ
8	0	0	33	41	53	1	110	98	-31	2	140	130	172	3	0	18	36
		4	45	48	-57	5	102	97	18	6	0	19	-1	7	54	50	-159
		8	0	13	-68	9	0	29	61								
8	1	0	46	43	-51	1	121	109	-159	2	207	185	138	3	251	251	-140
		4	69	62	-165	5	75	65	128	6	94	76	153	7	42	37	-129
		8	27	21	-22	9	56	42	34								
8	2	0	67	55	-70	1	98	90	36	2	54	59	129	3	84	81	-69
		4	45	37	-84	5	42	37	15	6	56	62	132	7	21	20	-11
		8	52	51	-98	9	18	17	121								
8	3	0	61	56	-57	1	0	11	154	2	27	23	141	3	64	63	154
		4	36	37	-62	5	41	44	-107	6	21	27	156	7	34	32	-128
		8	40	44	-125												
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		4	44	46	66	5	41	33	-103	6	23	20	115	7	0	11	144
		8	34	29	-3												
8	5	0	62	58	23	1	86	81	178	2	46	53	-128	3	114	103	-99
		4	68	63	24	5	23	22	-132	6	31	40	-120				
9	0	1	57	47	37	2	85	88	-4	3	39	34	176	4	91	79	-12
		5	73	67	19	6	62	47	-40	7	55	38	-111	8	33	29	-44
9	1	0	67	68	149	1	57	48	19	2	56	54	-127	3	86	72	175
		4	56	52	29	5	59	52	70	6	0	16	-16	7	18	16	-27
9	2	0	99	84	110	1	33	24	-98	2	96	96	-164	3	31	43	-40
		4	50	41	139	5	0	15	153	6	0	11	-54	7	45	29	-10
9	3	0	61	62	104	1	50	60	143	2	37	32	-141	3	52	52	6
		4	0	16	20	5	0	12	78								
9	4	0	33	25	129	1	23	27	170	2	42	36	-177	3	36	31	-99
		4	0	12	99												
9	5	0	37	26	138	1	63	57	-8	2	29	26	-146	3	73	50	-26
		4	33	29	63												
10	0	0	59	55	99	1	21	16	-15	2	27	18	-33	3	54	51	124
		4	42	30	-125	5	94	74	-43								
10	1	0	34	39	-12	1	40	44	-125	2	120	98	14	3	82	63	-115
		4	88	69	-1	5	34	25	-22								
10	3	0	59	43	73	1	47	29	15	2	58	43	-31	3	18	21	130
		4	25	27	-4												
10	4	0	31	28	123	1	33	32	-51	2	29	24	-149				

ABSTRACT OF THESIS

Name of Candidate ROBERT SIMPSON

Address 501, LANARK ROAD, JUNIPER GREEN, MIDLOTHIAN, EH14 5DQ

Degree Ph.D. *Date* 1971

Title of Thesis THE CRYSTAL STRUCTURE OF SOME DISACCHARIDES.

The crystal structures of α,α-trehalose dihydrate and 4,6;4',6'-di-O-ethylidene-α,α-trehalose monohydrate have been determined by X-ray diffraction techniques. In both cases three-dimensional X-ray intensity data were collected using an equi-inclination Weissenberg camera with Cu K_α radiation. The intensity measurements were made visually.

α,α-trehalose dihydrate was found to be orthorhombic, space group $P2_12_12_1$, with a = 12.233 Å, b = 17.889 Å, c = 7.596 Å and Z = 4. The observed and calculated densities were 1.512 and 1.511 $g.cm^{-3}$ respectively. The structure was solved by direct methods using the tangent formula. The atomic parameters were refined by the method of least squares to a final residual, R = 5.5%.

It was found that the molecules are held together by van der Waal's forces and by a complex network of twelve hydrogen bonds. One water molecule is trigonally and one tetrahedrally co-ordinate. The acetal oxygen atom in one residue only acts as an acceptor in a hydrogen bond, which is rather long at 2.88 Å. The molecule is in the expected conformation with the two glucopyranose rings in the "chair" form. The bond angle at the glucosidic linkage is 115.7°. The two crystallographically unrelated but chemically identical glucose residues are closely similar. The main effect of the different crystal packing of the two rings is to cause slight distortions of the atoms O(3) and O(4).

4,6;4',6'-di-O-ethylidene-α,α-trehalose monohydrate was found to be monoclinic, space group $P2_1$, with a = 11.276 Å, b = 8.435 Å, c = 10.004 Å, β = 97.58° and Z = 2. The observed and calculated densities were 1.452 and 1.445 $g.cm^{-3}$ respectively. The structure was solved by direct methods using the Σ_2

Use other side if necessary.

relationship. The atomic parameters were refined by the method of least squares to a final residual, R = 12.2%.

It was found that the molecules are held together by a network of six hydrogen bonds and by van der Waal's forces which are particularly strong between the methyl groups. The water molecule is trigonally co-ordinate. Two ethereal oxygen atoms act as acceptors in hydrogen bonds, which are both rather long at 2.83 and 2.88 Å. The six-membered rings closed by the ethylidene groups are parallel to the glucopyranoid rings and in the "chair" form. The methyl groups are in the equatorial position. The bond angle at the glucosidic linkage is 115.0°. The stereochemistry of this linkage is very similar to that in the α,α-trehalose molecule.